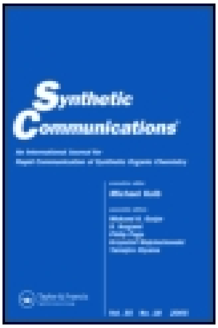

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Convenient Synthesis of 1,8-Diiodoanthracene and Its Coupling with Thianthrene Boronic Acids

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CONVENIENT SYNTHESIS OF 1,8-DIIODOANTHRACENE AND ITS COUPLING WITH THIANTHRENE BORONIC ACIDS

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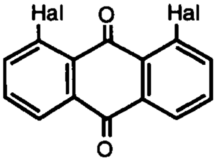
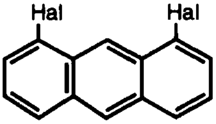
Abstract: 1,8-Diiodoanthracene has been prepared from commercially available 1,8-dichloroanthraquinone; it was shown to couple twice under Pd(0)-catalysis, with thianthrene 1- and 2-boronic acids giving 1,8-bis(thianthrenyl)anthracenes.

We are examining ways in which to construct molecules in which potentially electroactive substituents are placed in such a way as to be held close, and face to face, with the ultimate objective of examining electronic transmission between those substituents, possibly also, in some cases, involving the aromatic 'pillaring' unit to which they would be attached. We have for example shown[1] that two thianthrene units can be substituted for the chlorine atoms of 1,8-dichloroanthra-9,10-quinone, **1a**, using palladium(0) coupling procedures. We needed to carry out a comparable coupling with a suitable 1,8-dihalo-anthracene, for comparison with analogous thianthrenes,[2] however although the transformation of **1a** into 1,8-dichloroanthracene, **2b**, has been reported,[3] 1,8-diiodoanthracene, **2b**, which is required for efficient Pd(0) coupling, was not known.

1 Hal
a Cl
b I



2 Hal
a Cl
b I



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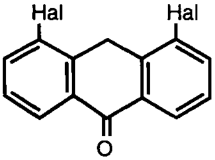
* To whom correspondence should be addressed.

1,8-Diiodo-9,10-anthraquinone, **1b**, has been previously prepared[4] *via* a 4-step sequence starting from the commercially available 1,8-dichloro-9,10-anthraquinone, **1a**: displacement of the halogens with toluene-*para*-sulfonamide, hydrolysis to the 1,8-diamine, then double diazotisation followed by a double Sandmeyer reaction formed the diiodide, **1b**, but with an overall yield on repetition in our hands of only 10% – the route is long and the Sandmeyer capricious. Following a sparsely detailed Russian patent,[5] we have been able to achieve the transformation of the dichloride into the diiodide directly, albeit in only 33% yield, in a one-pot procedure using sodium iodide in the presence of copper bronze.

Reduction of the diiodoanthraquinone proved difficult: application of the method[3] employed for the reduction of the dichloro-analogue to the anthracene (Zn/NH_3 then c. HCl), or the method[6] used to transform **1a** into the corresponding anthrone, **3a**, simply destroyed the starting diiodide; the diiodo-quinone was unaffected by sodium cyanoborohydride in acetic acid. However, sodium borohydride in methanol reduced **1b** giving diol **4**, from which, following a precedent,[7] and with the improvement of using a brief treatment with a little concentrated hydrochloric acid in methanol, produced a single anthrone, **3b**, with no trace of its isomer. These last two steps can be conveniently combined into a one-pot procedure, for addition of the acid both destroys excess borohydride and brings about the dehydration, though there is some loss in overall yield. The regiochemistry of the dehydration was established by *O*-methylation of **3b** followed by examination of the product, **5**, by ^1H NMR spectroscopy and the observation of an nOe effect between the *O*-methyl group and the 5-/6-protons.

3	Hal
a	Cl
b	I



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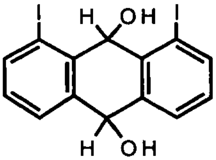
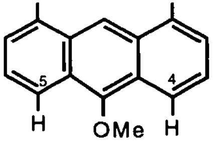
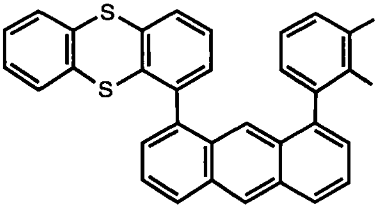


5

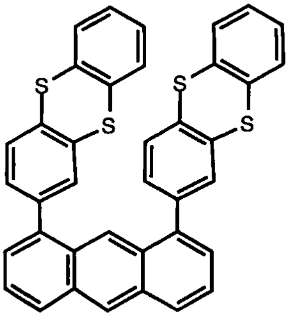


Finally, further reduction of the anthrone using sodium borohydride then acid-catalysed dehydration[8] of the resulting alcohol gave the target 1,8-diiodoanthracene, **2b**.

The potential for construction of more complex molecules was illustrated by the coupling of **2b** with thianthrene-1- and -2-boronic acids affording **6a** and **6b**, respectively.



6a



6b

EXPERIMENTAL

1,8-Diiodo-9,10-anthraquinone, 1b:- 1,8-dichloro-9,10-anthraquinone, **1a** (11.58 g, 41.8 mmol), sodium iodide (25.05 g, 167.1 mmol) and copper-bronze (0.8 g) were heated at reflux with mechanical stirring in nitrobenzene (40 ml) for 16 hours. Removal of solvent by steam distillation afforded an orange-brown solid which was crystallized from chlorobenzene to yield 1,8-diiodoanthraquinone, **1b** (6.34 g, 33%), m.p. 278-280 °C (lit.,[4] 282-283 °C) (Found: C, 36.8; H, 1.3; I 54.9. $C_{14}H_6I_2O_2$ requires C, 36.55; H, 1.3; I, 55.2%); λ_{max} (log ε_{max}) (DCM) 240 (4.33), 262 (4.43) and 366 (3.67) nm; υ_{max} (film)/cm^{-1} 2924, 1674, 1565, 1316, 1240, 1110, 799 and 729; δ_H(200 MHz; $CDCl_3$) 7.37 (2H, dd, *J* 7.7 and 7.7, 3- and 6-H), 8.29 (2H, dd, *J* 7.7 and 1.5, 4- and 5-H) and 8.40 (2H, dd, *J* 7.7 and 1.1, 2- and 7-H); *m/z* (CI) 478 (MNH_4^+, 100%), 461 (MH^+, 20%) and 195 (55%).

1,8-Diiodo-9,10-dihydroxy-9,10-dihydroanthracene, 4:- Sodium borohydride (206 mg, 5.43 mmol) was added, portionwise, over 15 minutes to a stirred suspension of 1,8-diiodoanthraquinone, **1b** (500 mg, 1.09 mmol) in AR methanol (25 ml) at room temperature. After addition was complete, stirring was continued for a further 15 minutes and then the solution was filtered into ice-water (~ 75 ml). The pale yellow-white precipitate was collected, washed and dried in air to give

1,8-diiodo-9,10-dihydroxy-9,10-dihydroanthracene, **4** (363 mg, 72%), m.p. 168-170 °C (Found: C, 36.8; H, 2.1; I 53.0%. $C_{14}H_{10}I_2O_2$ requires C, 36.2; H, 2.2; I, 54.7%); λ_{max} (log ε_{max}) (EtOH) 230 (4.37) and 268 (3.35) nm; υ_{max} (film)/cm^{-1} 3353 (OH), 1438, 1174, 1140 and 771; δ_H(200 MHz; CD_3OD) 5.93 (1H, s, 10-H), 6.37 (1H, s, 9-H), 7.09 (2H, dd, *J* 7.7 and 8.1, 3- and 6-H) and 7.81 (4H, m, 2- and 7-H, 4- and 5-H); *m/z* (EI) 446 (M^+ - H_2O, 65%), 319 (50%), 163 (100%) and 152 (60%).

4,5-Diiodo-9(10*H*)-anthracenone, 3b:- (a) To a solution of 1,8-diiodo-9,10-dihydroxy-9,10-dihydroanthracene, **4** (509 mg, 1.10 mmol) in methanol (25 ml) was added concentrated hydrochloric acid (2 ml). After heating and stirring at reflux for 1 hour the mixture was allowed to cool and the yellow precipitate collected, washed and dried in the air to give the *anthrone*, **3b** (414 mg, 85%). An analytical sample was crystallized from toluene to give yellow crystals m.p. 210-212 °C (Found: C, 37.75; H, 1.8; I, 56.9%. $C_{14}H_8I_2O$ requires C, 37.7; H, 1.8; I, 56.9%); λ_{max} (log ε_{max}) (DCM) 266 (4.18), 276 (4.16) and 308 (3.56) nm; υ_{max} (film)/cm^{-1} 1673, 1586, 1309, 1103, 944, 825 and 737; δ_H(300 MHz; $CDCl_3$) 4.09 (2H, s, CH_2) 7.30 (2H, dd, *J* 7.85 and 7.7, 3- and 6-H), 8.22 (2H, dd, *J* 7.7 and 1.1, 4- and 5-H) and 8.41 (2H, dd, *J* 7.85 and 1.1, 2- and 7-H); δ_C(75 MHz; $CDCl_3$) 183.40, 143.89, 142.33, 132.59, 128.98, 128.04, 101.08 and 46.44; *m/z* (CI) 464 (MNH_4^+, 15%), 447 (MH^+, 20%), 338 (30%), 321 (40%), 212 (35%) and 195 (100%).

(b) Sodium borohydride (412 mg, 10.89 mmol) was added, portionwise, over 15 minutes to a stirred suspension of 1,8-diiodo-9,10-anthraquinone, **1b** (1.00 g, 2.17 mmol) in AR methanol (50 ml) at room temperature. After addition was complete, stirring was continued for a further 60 minutes and then concentrated hydrochloric acid (4 ml) was added. The reaction mixture was heated at reflux for 60 minutes and the yellow precipitate was collected, washed with water and dried to give 4,5-diiodo-9(10*H*)-anthracenone (350 mg, 36%)

1,8-Diiodo-10-methoxyanthracene, 5:- A solution of 4,5-diiodo-9(10*H*)-anthracenone, **3b** (50 mg, 0.112 mmol) and dimethyl sulphate (57 mg, 0.04 ml, 0.448 mmol) in dichloromethane (4 ml) was added dropwise over 15 minutes to a stirred solution of sodium hydroxide (250 mg, 6.25 mmol) and tetrabutylammonium bromide (10 mg, 0.031 mmol) in water (2 ml). After stirring for 1.5 hours the red coloured organic phase had changed colour to orange. The organic phase was separated, washed with water (2 x 5 ml) and brine (1 x 5 ml), dried ($MgSO_4$) and solvent removed *in vacuo* to yield a yellow crystalline solid which was recrystallized from toluene to give pure *1,8-diiodo-10-methoxyanthracene*, **5** (47 mg, 92%), m.p. 191-193 °C (Accurate mass: found 459.8822. $C_{15}H_{10}I_2O$ requires 459.8821); λ_{max} (log ε_{max}) (DCM) 262 (4.78), 352 (3.59), 368 (3.88), 386 (4.06) and 408 (3.98) nm; υ_{max} (film)/cm^{-1} 2360, 2342, 1333, 1092, 855, 809 and 731; δ_H(300 MHz; $CDCl_3$) 4.13 (3H, s, Ar-OCH_3), 7.21 (2H, dd, *J* 8.7 and 7.1, 3- and 6-H), 8.17 (2H, d, *J* 7.1, 4- and 5-H), 8.31 (2H, d, *J* 8.7, 2- and 7-H) and 8.80 (1H, s, 9-H); δ_C(75 MHz; $CDCl_3$) 153.06, 138.07, 133.52, 132.72, 126.58, 125.00, 123.26, 100.56 and 63.79; *m/z* (CI) 478 (MNH_4^+, 5%) and 461 (MH^+, 100%).

1,8-Diiodoanthracene, 5:- 4,5-Diiodo-9(10*H*)-anthracenone, **3b** (350 mg, 0.78 mmol) was suspended in diglyme (10 ml) and the mixture was stirred and flushed with nitrogen for 15 minutes. Sodium borohydride (175 mg, 4.63 mmol) was added and after 30 minutes methanol (5 ml) was added followed by another portion of sodium borohydride (75 mg, 1.98 mmol). The orange-red solution was stirred at room temperature overnight and then glacial acetic acid was added to bring the pH to 3-4, followed by concentrated hydrochloric acid to pH < 2. After stirring at room temperature for 60 minutes, water was added and the resulting yellow precipitate collected, washed and dried. Purification by flash chromatography on silica gel with light petroleum (b.p. 40-60 °C) as the eluent gave *1,8-diiodoanthracene*, **1b**, as a pale yellow solid (130 mg, 39%), m.p. 201-202 °C (Accurate mass: found 429.8721. $C_{14}H_8I_2$ requires 429.8719); λ_{max} (log ε_{max}) (DCM) 256 (4.71), 340 (3.57), 356 (3.88), 376 (4.05) and 396 (4.00) nm; υ_{max} (film)/cm^{-1} 1664, 1309, 1165, 1102, 1034 and 734; δ_H(200 MHz; $CDCl_3$) 7.20 (2H, t, *J* 8.4, 3- and 6-H), 8.01 (2H, d, J 8.4, 4- and 5-H), 8.16 (2H, d, *J* 7.3, 2- and 7-H), 8.32 (1H, s, 10-H) and 8.95 (1H, s, 9-H); *m/z* (EI) 430 (M^+, 100%), 304 (25), 303 (20) and 176 (70).

1,8-Bis(thianthren-1-yl)anthracene, 6a:- 1,8-Diiodoanthracene, **2b** (100 mg, 0.233 mmol) and tetrakis(triphenylphosphine)palladium(0) (20 mg, 0.017 mmol) were stirred together in dimethoxyethane (10 ml) under a nitrogen atmosphere for

10 minutes at room temperature. Thianthrene-1-boronic acid[2] (500 mg, 1.92 mmol) was added, immediately followed by aqueous sodium hydrogen carbonate solution (1M, 1.40 ml, 1.4 mmol). The reaction mixture was heated at reflux for 24 hours, with vigorous stirring under nitrogen. Solvent was removed *in vacuo*, water (15 ml) was added and the residue was extracted with dichloromethane (3 x 10 ml). The combined organic phases were washed with water, brine and dried ($MgSO_4$). After removal of the solvent *in vacuo*, the product was purified by flash chromatography on silica gel with ethyl acetate-light petroleum (b.p. 40-60 °C) (1:9) as the eluent to yield *1,8-bis(thianthren-1-yl)anthracene*, **6a**, as a pale yellow solid (33 mg, 23%), m.p. 296-298 °C (Accurate mass: found 606.0603. $C_{38}H_{22}S_4$ requires 606.0604); λ_{max} (log ε_{max}) (DCM) 256 (4.73), 336 (3.38), 354 (3.64), 372 (3.80) and 390 (3.74); υ_{max} (film)/cm^{-1} 3050, 2923, 1446, 1432, 1392, 1162, 1108, 1029 and 742; δ_H(200 MHz; $CDCl_3$) 6.79-7.61 (19H, m, Ar-H), 8.14 (2H, d, *J* 8.4, Ar-H) and 8.62 (1H, s, Ar-H); *m/z* (CI) 624 (MNH_4^+, 100%), 607 (MH^+, 25), 279 (60) and 178 (50).

1,8-Bis(thianthren-2-yl)anthracene, 6b:- 1,8-Diiodoanthracene, **2b** (100 mg, 0.233 mmol) and tetrakis(triphenylphosphine)palladium(0) (20 mg, 0.017 mmol) were stirred together in dimethoxyethane (10 ml) under a nitrogen atmosphere for 10 minutes at room temperature. Thianthrene-2-boronic acid[2] (240 mg, 0.923 mmol) was added, immediately followed by aqueous sodium hydrogen carbonate solution (1M, 1.40 ml, 1.4 mmol). The reaction mixture was heated at reflux for 24 hours, with vigorous stirring under nitrogen. Solvent was removed *in vacuo*, water (15 ml) was added and the residue was extracted with dichloromethane (3 x 10 ml). The combined organic phases were washed with water, brine and dried ($MgSO_4$). After removal of the solvent *in vacuo*, the product was purified by flash chromatography on silica gel with ethyl acetate-light petroleum (b.p. 40-60 °C) (1:9) as the eluent to yield *1,8-bis(thianthren-2-yl)anthracene*, **6b**, as a pale yellow solid (110 mg, 78%), m.p. 148-150 °C (Accurate mass: found 606.0605. $C_{38}H_{22}S_4$ requires 606.0604); λ_{max} (log ε_{max}) (DCM) 264 (5.12), 362 (3.91), 380 (4.10) and 400 (4.03) nm; υ_{max} (film)/cm^{-1} 3050, 2926, 1442, 1262, 1107, 1033, 876 and 746; δ_H(200 MHz; $CDCl_3$) 7.24-7.62 (18H, m, Ar-H), 8.03 (2H, d, *J* 8.0, Ar-H) and 8.55 (2H, d, *J* 8.0, Ar-H); *m/z* (CI) 624 (MNH_4^+, 100%), 607 (MH^+, 10), 447 (48) and 279 (50).

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