Approaches to the stepwise synthesis of benzoporphyrins and phthalocyanines. Part 1. Synthesis of *opp*-dibenzoporphyrins (dibenzo[*g*,*q*]porphyrins)

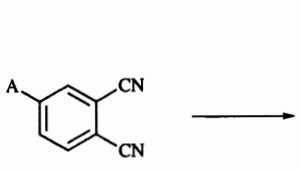
Raymond Bonnett and Kimberly A. McManus

Chemistry Department, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK

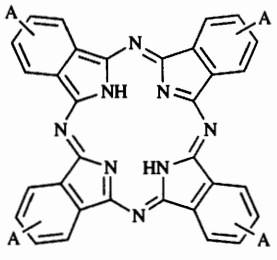
A stepwise synthesis of the *opp*-dibenzoporphyrin (dibenzo[*g*,*q*]porphyrin) system involving isoindole precursors is described. 3-Halogeno-1-formylisoindoles are condensed with various α-unsubstituted pyrroles to give the corresponding benzopyrromethene hydrobromides. Thermal self-condensation of such compounds bearing an α-methyl group gives the corresponding *opp*-dibenzoporphyrin derivatives in low to modest yields depending on the β-substitution pattern of the original pyrrole component.

Commercial interest in the phthalocyanine system was originally confined essentially to the striking pigmentary properties of these substances. However, in recent years this interest has expanded and diversified with the development of electro-optical, molecular electronic and photodynamic therapy applications.[1] The chemistry of allied macrocycles, such as the porphyrazines and benzoporphyrins, has been relatively neglected, although these systems would also be expected to display commercial potential.

From the point of view of synthetic versatility, the problem with the phthalocyanines is that the methods currently available do not allow the construction of unsymmetrically substituted molecules at will. This is in marked contrast with porphyrin synthesis (see Scheme 1 in which the various synthetic approaches are classified) where stepwise syntheses leading to unsymmetrically substituted porphyrins *via* linear tetrapyrrole intermediates are well developed (1 × 4, Class A in Scheme 1).[2] The syntheses of phthalocyanines are, in contrast, almost medieval, following the Class C route (4 × 1, Scheme 1), which amounts to a reductive cyclotetramerisation of a phthalonitrile derivative. The substituents on the benzenoid rings are necessarily the same and, if the phthalonitrile is mono (or unsymmetrically) substituted, as at **1**, then in the absence of overwhelming steric direction, the product is expected to comprise the four 'type' (*i.e.* positional) isomers, as at **2**. Related



1
or phthalamide, phthalimide, or diiminoisoindoline analogues



2 Four type isomers

problems arise in the porphyrin series, for example with the important Rothemund synthesis of *meso*-tetraarylporphyrins.† In that series a stepwise synthesis has been devised to allow the preparation of compounds with four different aryl groups.[3]

Several ingenious methods for circumventing the problem of the inflexibility of the 4 × 1 synthesis of phthalocyanines have been described. They include (i) a mixed condensation involving two phthalonitriles, one in excess, and the other substituted with a solubilising substituent,[7] (ii) a Merrifield-type synthesis in which one of the phthalonitriles in a mixed condensation is differentiated by being attached (reversibly) to a polymer,[8] and (iii) the macroring-expansion of chloroboron(III) subphthalocyanine with a substituted phthalonitrile.[9] While of considerable chemical interest, such approaches do not afford the flexibility available in the porphyrin series.

It seems to us that it should be feasible to develop syntheses using isoindole units, rather than pyrrole units, leading to phthalocyanine and benzoporphyrin systems (Scheme 2). Because the stepwise synthesis of the nitrogen bridges affords special challenges of its own, we have set out by trying to synthesise benzoporphyrin derivatives from isoindoles in a stepwise manner.

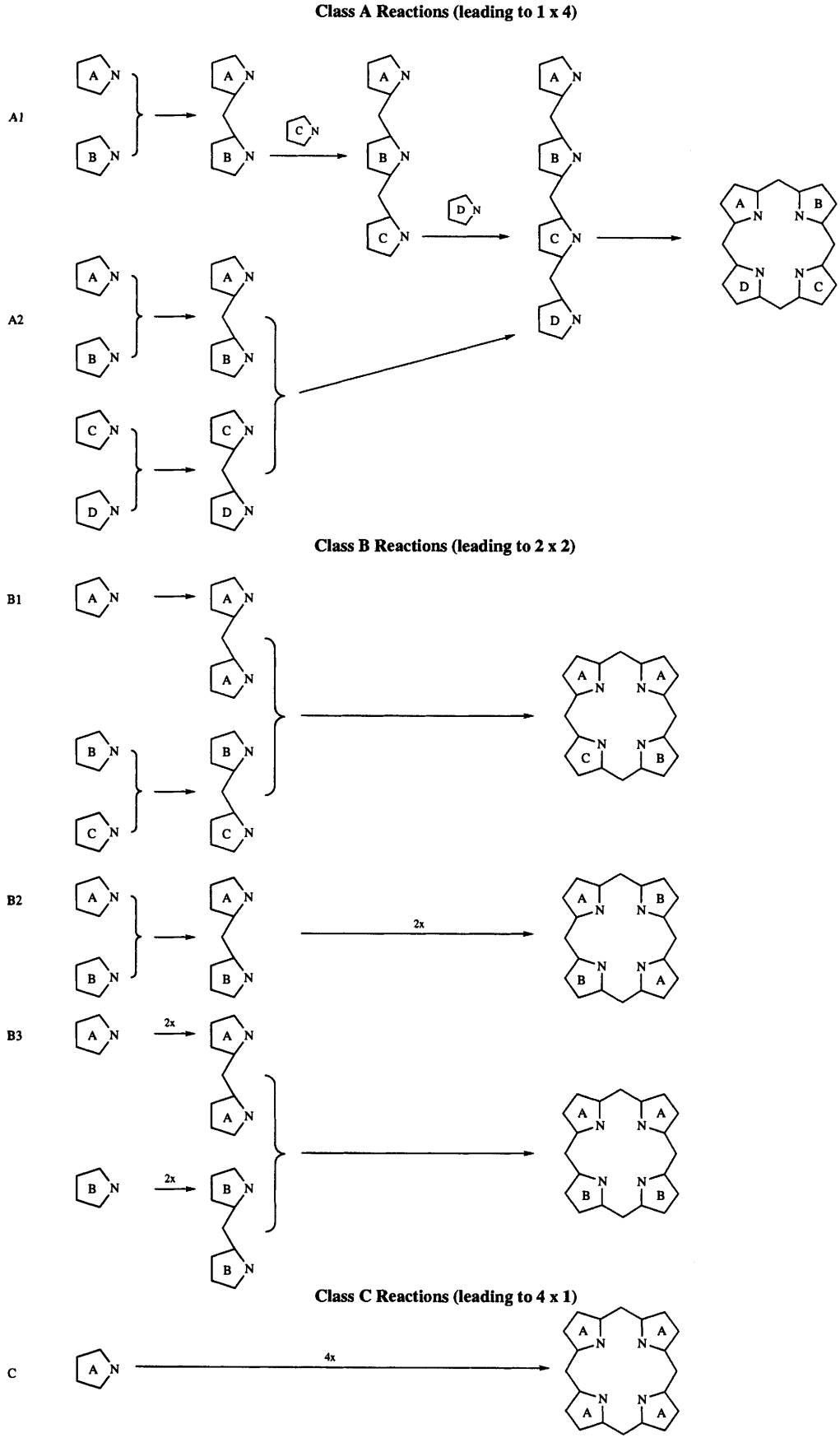
Tetrabenzoporphyrins have generally been prepared in the past from phthalimidine derivatives,[10] but two syntheses from true isoindoles have been described.[11,12] All of these syntheses are of the 4 × 1 (Class C) variety. Benzoporphyrins and tetrahydrobenzoporphyrins have been detected in trace amounts in various oil shales,[13] and stepwise syntheses of such compounds from *pyrrole* intermediates have been reported.[14,15] Here we describe a route to dibenzoporphyrins with the benzenoid rings on opposite pyrroles (hence, *opp*-dibenzoporphyrins) using a 2 × 2 route (Class **B2** in Scheme 1).[16]

Benzopyrromethene hydrobromides

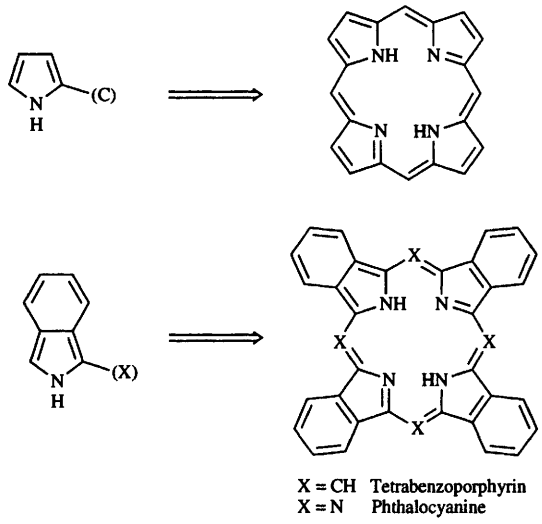
The key synthon in this approach is the known[17] 3-haloisoindole-1-carbaldehyde **3**. This is prepared by a double Vilsmeier reaction from phthalimidine **4** using phosphorus oxyhalide and dimethylformamide (Scheme 3). The haloformylisoindoles **3** are sensitive compounds, and are best used without delay.

Condensation of **3** with an α-unsubstituted pyrrole (or an α-carboxypyrrole) under acidic conditions in the cold then produces novel benzopyrromethene salts as reddish-purple crystalline solids. Typical reaction conditions employ ethanol–hydrogen bromide at 0 °C, crystalline precipitates being formed on keeping the reaction mixture overnight at −20 °C. Benzopyrromethene hydrobromides were obtained in yields ranging from 11–50% as shown in Table 1. Yields have not been optimised. The lowest yield was observed with a β-ethoxycarbonyl substituent on the pyrrole. In one example starting with an α-carboxylic acid (rather than an α-unsubstituted pyrrole) a

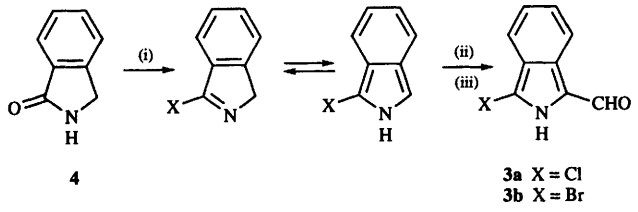
† The *meso* positions are the 5, 10, 15 and 20 positions and the β positions are the 2, 3, 7, 8, 12, 13, 17 and 18 positions.



Scheme 1 Classification of synthetic approaches to the porphyrin skeleton. For clarity only the elemental framework is displayed, so that, for example, the *meso* bridges may be sp^3 or sp^2. Developed from Evstigneeva,[4] Mironov[5] and Salgado.[6] The same classification scheme may be used to refer to approaches to porphyrazines, phthalocyanines and benzoporphyrins, it being understood that only the pyrrolic ring is represented, and the bridge may be C or N.



Scheme 2



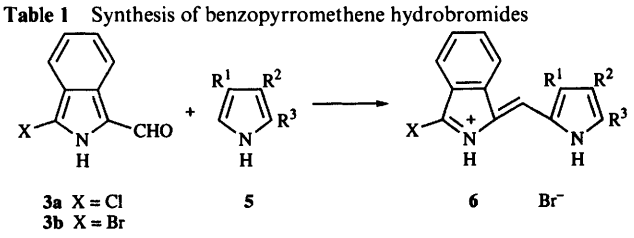
Scheme 3 *Reagents*: i, POX_3; ii, POX_3–DMF; i + ii, one pot reaction; iii, NaOH, aq. EtOH

modest yield (45%) was recorded. Structural assignments rest on elemental analyses, ^1H and ^{13}C NMR spectra, and mass spectra. In the electron impact mass spectra the free base generally appears as the base peak.

Thus condensation of 3-chloroisoindole-1-carbaldehyde **3a** with 2,4-dimethylpyrrole **5a** gave the reddish-purple benzopyrromethene hydrobromide **6a** in 38% yield. In dilute alcoholic solution the salt was partially converted into the free base form, so in order to maintain the product in the protonated form, the visible spectrum was recorded in dichloromethane acidified with hydrogen bromide–acetic acid, when an absorption maximum was observed at 530 nm (ε/l mol^{-1} cm^{-1} 105 000), showing the expected bathochromic shift with respect to pyrromethene salts (λ_{max} *ca.* 480 nm) due to the extra conjugation. The ^1H NMR spectrum showed the two pyrrolic methyl groups (δ 2.43 and 2.56), the β-pyrrolic proton (δ 6.09) and the bridge proton at lower field (δ 7.43). The protons on the nitrogens appeared well downfield at δ 13.14 and 13.90. These shifts are comparable with those recorded for similar pyrromethene salts.[18] The ^{13}C NMR spectrum showed signals for all the carbon atoms, with the correct splittings. In the electron impact mass spectrum the base peak (*m*/*z* 256) corresponded to the free base. The infrared spectrum showed a peak at 749 cm^{-1} corresponding to the out-of-plane C–H deformation associated with the *ortho*-substituted benzene ring.

Elemental analysis of **6a** was satisfactory, but analysis of some of the hydrobromides suggested that partial loss of hydrogen bromide had occurred during the drying of the analytical sample. In the mass spectrum of **6d**, two additional ions were observed (above M – HBr) at *m*/*z* 330 and 328. We attribute these to the displacement of the 1-chloro group by bromide (from HBr) in the mass spectrometer inlet system. There were some indications that the 1-bromo-3-formylisoindole was a more satisfactory precursor than the corresponding chloro compound. Thus with pyrroles **5e** and **5f** the condensation reaction was successful with the former reactant, but not with the latter.

Table 1 Synthesis of benzopyrromethene hydrobromides

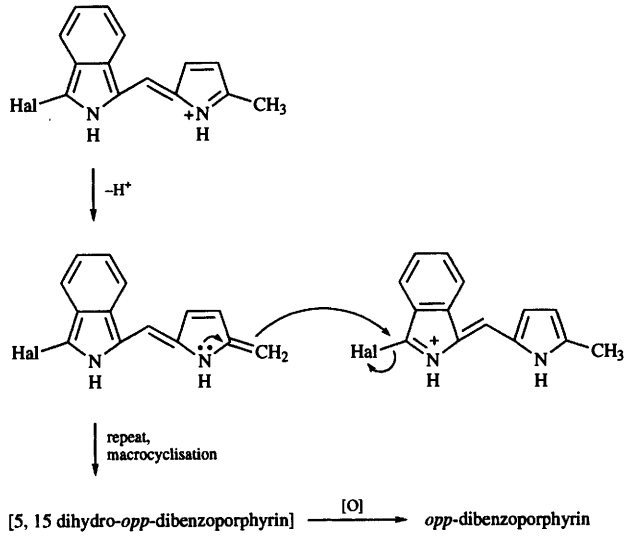


Isoindole	Pyrrole	Benzopyrromethene hydrobromide	Yield (%)
3a	**5a**	**6a**, X = Cl	38
3a	**5b**	**6b**, X = Cl	25
3a	**5c**	**6c**, X = Cl	22
3a	**5d**	**6d**, X = Cl	22
3b	**5a**	**6a**, X = Br	18
3b	**5e**	**6e**, X = Br	25
3b	**5d**	**6d**, X = Br	31
3b	**5c**	**6c**, X = Br	50
3b	**5f**	**6f**, X = Br	11
3b	**5g**	**6g**, X = Br	45

For **5a**, **6a** $R^1 = R^3 = Me$, $R^2 = H$
5b, **6b** $R^1 = Et$, $R^2 = R^3 = Me$
5c, **6c** $R^1 = R^3 = Me$, $R^2 = Et$
5d, **6d** $R^1 = R^2 = Et$, $R^3 = H$
5e, **6e** $R^1 = R^2 = Me$, $R^3 = H$
5f, **6f** $R^1 = R^3 = Me$, $R^2 = CO_2Et$
5g, **6g** $R^1 = R^2 = R^3 = Me$ (**5g** as 2-COOH)

opp-Dibenzoporphyrins

The benzopyrromethene hydrobromides **6** possessing a methyl group at R^3 appeared to be suitable precursors for the synthesis of *opp*-dibenzoporphyrins in a thermally-initiated reaction of Class B2 (Scheme 1). The reaction envisaged is shown in Scheme 4. It was found that heating suitably substituted

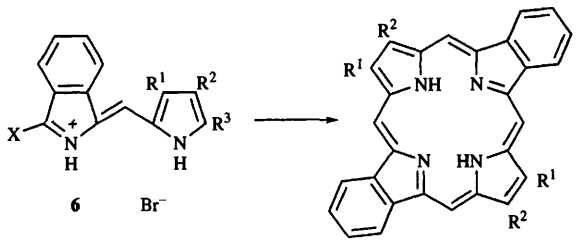


Scheme 4

benzopyrromethene hydrobromides in *o*-dichlorobenzene at 196 °C for 3–6 h gave low to modest yields of the expected *opp*-dibenzoporphyrins (Table 2). The progress of the reaction could be monitored by visible spectroscopy. The products were characterised by accurate mass measurement of the molecular ion, by ^1H NMR spectroscopy, and by visible spectroscopy. The visible spectra showed a strong band I in the 650 nm region (ε/l mol^{-1} cm^{-1} *ca.* 25 000), which makes these chromophores potentially attractive candidates as photosensitisers for photodynamic therapy.[19]

The synthesis was moderately successful in the preparation of 2,12-diethyl-3,13-dimethyl-*opp*-dibenzoporphyrin, **7b**, which is

Table 2 Synthesis of *opp*-dibenzoporphyrins



6 Br⁻ 7

6, R^3 = Me	*opp*-Dibenzoporphyrin 7	Yield (%)
6a, X = Cl	R^1 = Me, R^2 = H (**7a**)	4
6a, X = Br	R^1 = Me, R^2 = H (**7a**)	4
6b, X = Cl	R^1 = Et, R^2 = Me (**7b**)	54
6c, X = Cl	R^1 = Et, R^2 = Me (**7b**)	31
6g, X = Br	R^1 = Me, R^2 = Me (**7c**)	5

a known compound. This was obtained in 54% yield from the chlorobenzopyrromethene salt **6b** (X = Cl) and in 31% yield from the isomeric chlorobenzopyrromethene salt **6c** (X = Cl). With the bromobenzopyrromethene salt **6c** (X = Br) as the precursor, the reaction proceeded more rapidly, but the isolated yield was little changed. The spectroscopic properties of the product accorded with those reported,[14] and there was no evidence that randomisation had occurred during the reaction.

Much less successful reactions were observed when the pyrrole unit had a free β-position, the reaction **6a** (X = Cl) ⟶ **7a** proceeding in only 4% yield. This illustrates a well known tendency for the synthesis of β-unsubstituted porphyrins to proceed in low yield,[20] presumably because the free β-position offers a site at which alternative processes may occur, leading, for example, to polymeric material. The tetramethyl compound **7c** was also obtained in low yield (5%): in this case, the difficulty is ascribed to its very low solubility which made purification difficult.

Although it is clear that much remains to be done to develop satisfactory methods for linking isoindoles to one another and to pyrroles through carbon and nitrogen bridges, the principle of using isoindoles in a rational stepwise approach, which we regard as a first stage, has been demonstrated.

Experimental

General

The following spectroscopic equipment was used. ^{1}H and ^{13}C NMR spectra: Bruker AM250 or AMX600, chemical shifts (δ) being given relative to tetramethylsilane and J values in Hz; IR spectra: Perkin-Elmer 1600 FT; UV–VIS spectra: Perkin-Elmer Lambda 2, extinction coefficients being given in l mol^{-1} cm^{-1}; rel. A = relative absorbance; electron impact mass spectra: Kratos MS50. Thin layer chromatography was carried out on Merck Kieselgel 60H. Elemental analyses were performed by Microanalytical Services, University College, London. Melting points were determined on a Kofler block or by differential scanning calorimetry (DSC) and are not corrected.

3-Chloroisoindole-1-carbaldehyde 3a

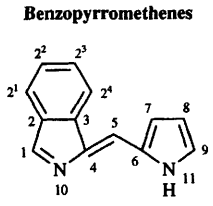
This was prepared following the method of von Dobeneck *et al.*[17] as follows. The corresponding bromo compound **3b** was made analogously.

All apparatus was flame dried. A mixture of dimethylformamide (dry, 8.5 ml, 8.0 g) and chloroform (dry, freshly distilled, 20 ml) was cooled to 0 °C with vigorous mechanical stirring. A solution of phosphorus oxychloride (9.2 ml, 15.1 g) in chloroform (dry, freshly distilled, 39 ml) was added dropwise at this temperature. A solution of 1,3-dihydroisoindol-1-one (phthalimidine) (6.6 g) in chloroform (dry, freshly distilled, 195 ml) was then added dropwise at 0 °C. The deep brown mixture was refluxed for 5 h and cooled. Chloroform (116 ml) was added and, at 0 °C, aqueous sodium hydroxide (5 M) was added to pH 8. The organic layer was washed three times with water and dried ($MgSO_4$). The product was concentrated, and chromatographed on alumina with chloroform. The first major fraction (greenish) was collected and the solvent removed to give the chloroenamine intermediate (3-chloro-1-dimethylaminomethylidene-1*H*-isoindole) as a discoloured solid (3.5 g). This intermediate was refluxed for 3 h in ethanol (210 ml) containing aqueous sodium hydroxide (4 M, 17 ml). The solution was neutralised with 2 M HCl at 0 °C, when a white crystalline precipitate of 3-chloroisoindole-1-carbaldehyde was formed. The crystals were washed several times with ice–water, and dried. The material became discoloured on manipulation. Yield 2.7 g (30%); mp *ca.* 126 °C (decomp.) [lit.,[17] 126 °C (decomp.)].

The ^{1}H NMR spectrum was not identical with that reported [in $(CD_3)_2SO$][17] and is assigned as follows: δ_H[250 MHz, $CDCl_3$–$(CD_3)_2SO$] 7.20, 7.37 (each dd, arom. 5-, 6-H), 7.65 (d, J 8.4, arom. 4-H), 7.92 (br d, J 7.8, arom. 7-H), 9.81 (s, CHO) and 10.80 (v br, NH, D_2O exchanged).

Benzopyrromethenes

Numeration based on IUPAC rule TP-7.2, but with retention of pyrromethene (rather than dipyrrin) as a trivial name for the skeleton.[21] In all the examples presented here, 'benzo' means 2,3-benzo.



1-Chloro-7,9-dimethylbenzopyrromethene hydrobromide 6a (X = Cl). 3-Chloroisoindole-1-carbaldehyde **3a** (81 mg, 0.45 mmol) and 2,4-dimethylpyrrole (42 mg, 0.44 mmol) in ethanol (4 ml) at 0 °C was stirred and treated with 48% HBr in water (0.1 ml). The mixture was kept at −10 °C overnight. The reddish-purple precipitate was filtered off and washed with cold ethanol containing HBr and dried *in vacuo* at 70 °C, to give 57 mg (38%) of the *benzopyrromethene hydrobromide* **6a** (X = Cl), mp 126–128 °C (by DSC) (Found: C, 53.25; H, 4.15; N, 8.0%. $C_{15}H_{14}N_2ClBr$ requires C, 53.35; H, 4.2; N, 8.3%); λ_{max}-(CH_2Cl_2, 1.3 M in HBr–HOAc)/nm (ε) 498 (30 500) and 530 (105 000); ν_{max}(KBr)/cm^{-1} 3029 (m), 2855 (m), 2659 (m), 1621 (s), 1561 (m), 1278 (m), 1250 (s), 967 (s), 814 (m) and 749 (m); δ_H(250 MHz, $CDCl_3$) 2.43, 2.56 (both s, 7- and 9-Me), 6.09 (s, 8-H), 7.43 (s, 5-H), 7.45, 7.65 (both dd, 2^2- and 2^3-H), 7.77 (d, J 8.1, 2^1-H), 7.96 (d, J 8.2, 2^4-H), 13.14 and 13.90 (both br s, 2 × NH); δ_C(62.9 MHz, $CDCl_3$–CF_3CO_2D) 12.35 (q, J 47, Me), 14.27 (q, J 49, Me), 116.3 (d, J 92.9, CH), 117.2 (d, J 97.8, CH), 119.2 (d, J 103.7, CH), 120.0 (s), 121.9 (d, J 105.4, CH), 125.9 (s), 126.6 (s), 127.0 (d, J 100.4, CH), 132.0 (d, J 102.6, CH), 136.6 (s), 139.4 (s), 145.1 (s) and 154.1 (s); *m/z* 258 (33%), 257 (26), 256 (100, M − HBr), 255 (31), 220 (41), 219 (24), 217 (24), 163 (22), 155 (31) and 151 (46).

The following hydrobromides were prepared in an analogous manner. Media for spectroscopic observations were as above, unless otherwise stated.

1-Chloro-7-ethyl-8,9-dimethylbenzopyrromethene hydrobromide 6b (X = Cl). Prepared from 4-ethyl-2,3-dimethylpyrrole **5b**, purple solid, 25%, decomp. 127 °C (DSC) (Found: C, 55.15; H, 4.7; N, 7.35%. $C_{17}H_{18}N_2ClBr$ requires C, 55.85; H, 4.95; N, 7.65%); λ_{max}(KBr)/nm (ε) 503 (33 200) and 537 (107 000);

ν_{max}/cm^{-1} 1623 (s), 1559 (m), 1412 (m), 1318 (m), 1286 (m), 1246 (s), 1154 (m), 1114 (m), 1051 (m), 973 (m), 956 (m), 858 (m), 817 (m), 743 (m), 673 (m) and 617 (m); δ_H(250 MHz) 1.22 (t, *J* 7.6, 7-CH_2CH_3), 1.99, 2.59 (both s, 8- and 9-Me), 2.75 (q, *J* 7.6, 7-CH_2CH_3), 7.39 (s, 5-H), 7.44, 7.63 (both dd, 2^2- and 2^3-H), 7.79 (d, *J* 8.2, 2^1-H), 7.93 (d, *J* 8.3, 2^4-H), 13.25 and 13.92 (both br s, 2 × NH); *m/z* 286 (35%), 285 (20), 284 (100, M − HBr), 269 (35), 248 (57) and 175 (67).

1-Chloro-8-ethyl-7,9-dimethylbenzopyrromethene hydrobromide 6c (X = Cl). Prepared from 3-ethyl-2,4-dimethylpyrrole **5c**, purple solid, 22%, decomp. 131 °C (DSC) (Found: C, 55.6; H, 5.15; N, 7.4%); λ_{max}($CHCl_3$)/nm (ε) 506 (33 000) and 537 (118 000); ν_{max}(KBr)/cm^{-1} 1621 (s), 1250 (s), 961 (m) and 749 (m); δ_H(250 MHz) 1.09 (t, *J* 7.6, 8-CH_2CH_3), 2.34, 2.60 (both s, 7- and 9-Me), 2.43 (q, *J* 7.6, 8-CH_2CH_3), 7.40 (s, 5-H), 7.43, 7.62 (both dd, 2^2- and 2^3-H), 7.78 (d, *J* 8.2, 2^1-H), 7.92 (d, *J* 8.3, 2^4-H), 13.24 and 13.93 (both br s, 2 × NH); *m/z* 286 (33%), 285 (22), 284 (100, M − HBr), 283 (12), 271 (15), 269 (20), 248 (12) and 233 (12).

1-Chloro-7,8-diethylbenzopyrromethene hydrobromide 6d (X = Cl). Prepared from 3,4-diethylpyrrole **5d**, dark purple solid, 22%, decomp. 174 °C (DSC) (Found: C, 60.1; H, 5.2; N, 8.0%. $C_{17}H_{17}N_2Cl$·0.68HBr requires C, 60.1; H, 5.25; N, 8.25%); λ_{max}/nm (ε) 502 (29 000) and 533 (82 000); ν_{max}/cm^{-1} 2953 (m), 1605 (s), 1398 (m), 1278 (s), 1239 (m), 1152 (m), 1038 (m), 929 (m), 793 (m) and 744 (m); δ_H(250 MHz) 1.22, 1.24 (both t, *J* 7.6, 2 × CH_2CH_3), 2.49, 2.76 (both q, *J* 7.6, 2 × CH_2CH_3), 7.47–7.53 (composite, 3 H, isoindole H, 5-H, pyrrole H), 7.69 (dd, isoindole H), 7.77 (d, *J* 8.1, 2^1-H), 7.95 (d, *J* 8.2, 2^4-H), 13.22 and 13.68 (both br s, 2 × NH); *m/z* 330 (31%), 328 (30), 284 (67, M − HBr), 269 (30), 249 (36), 248 (51), 233 (21), 219 (14) and 218 (10).

1-Bromo-7,9-dimethylbenzopyrromethene hydrobromide 6a (X = Br). Prepared from 2,4-dimethylpyrrole **5a** and **3b**, dark purple solid (18%) (small scale experiment: the product was not characterised but converted directly into porphyrin **7a**).

1-Bromo-7,8-dimethylbenzopyrromethene hydrobromide 6e (X = Br). Prepared from 3,4-dimethylpyrrole **5e** and **3b**, dark purple solid, 25%, decomp. 198 °C (DSC) (Found: C, 51.8; H, 3.9; N, 7.7%. $C_{15}H_{13}N_2Br$·0.60HBr requires C, 51.5; H, 3.9; N, 8.0%); λ_{max}/nm (ε) 504 (27 000) and 540 (79 000); ν_{max}(KBr)/cm^{-1} 1702 (m), 1614 (s), 1525 (m), 1467 (m), 1390 (m), 1320 (m), 1279 (s), 1261 (s), 1214 (m), 1155 (s), 1108 (m), 1049 (m), 914 (m), 791 (m), 744 (m) and 703 (m); δ_H(250 MHz) 2.07, 2.33 (both s, 7- and 8-Me), 7.47–7.53 (composite, 3 H, isoindole H, 5-H, pyrrole H), 7.69 (dd, isoindole H), 7.78 (d, *J* 8.1, 2^1-H), 7.96 (d, *J* 8.3, 2^4-H), 13.27 and 15.47 (both br s, 2 × NH); *m/z* 303 (17), 302 (98, M − HBr), 301 (50) and 300 (100, M − HBr).

1-Bromo-7,8-diethylbenzopyrromethene hydrobromide 6d (X = Br). Prepared from 3,4-diethylpyrrole **5d** and **3b**, dark purple solid, 31%, decomp. 173 °C (DSC) (Found: C, 53.6; H, 4.55; N, 7.1%. $C_{17}H_{17}N_2Br$·0.65HBr requires C, 53.5; H, 4.65; N, 7.34%); λ_{max}/nm (ε) 502 (29 500) and 536 (81 500); ν_{max}(KBr)/cm^{-1} 1610 (s), 1600 (s), 1401 (m), 1281 (s), 1239 (m), 1150 (m), 1040 (m), 930 (m), 794 (m) and 747 (m); δ_H(250 MHz) 1.20, 1.23 (both t, *J* 7.6, 2 × CH_2CH_3), 2.46, 2.79 (both q, *J* 7.6, 2 × CH_2CH_3), 7.46–7.53 (composite, 3 H, isoindole H, 5-H, pyrrole H), 7.72 (dd, isoindole H), 7.75 (d, *J* 8.1, 2^1-H), 8.01 (d, *J* 8.2, 2^4-H), 13.25 and 13.92 (both br s, 2 × NH); *m/z* 331 (19), 330 (100, M − HBr) and 328 (98, M − HBr).

1-Bromo-8-ethyl-7,9-dimethylbenzopyrromethene hydrobromide 6c (X = Br). Prepared from 3-ethyl-2,4-dimethylpyrrole **5c** and **3b**, purple solid, 50%, decomp. 129 °C (DSC) (Found: C, 49.8; H, 4.35; N, 6.6%. $C_{17}H_{18}N_2Br_2$ requires C, 49.8; H, 4.4; N, 6.85%); λ_{max}/nm (ε) 505 (30 600) and 540 (116 000); ν_{max}(KBr)/cm^{-1} 1626 (s), 1605 (s), 1270 (s), 1254 (s), 1155 (m), 1055 (m), 961 (m) and 741 (m); δ_H(250 MHz) 1.08 (t, *J* 7.6, 8-CH_2CH_3, 2.35, 2.56 (both s, 2 × Me), 2.41 (q, *J* 7.6, 8-CH_2CH_3), 7.41 (s, 5-H), 7.43, 7.61 (both dd, 2^3- and 2^3-H), 7.71 (d, *J* 8.2, 2^1-H), 7.93 (d, *J* 8.3, 2^4-H), 13.29 [br s, NH at 11 (from COSY experiment)], 14.00 [br s, NH at 10 (from COSY experiment)]; *m/z* 331 (19), 330 (100, M − HBr), 329 (29) and 328 (99, M − HBr).

1-Bromo-8-ethoxycarbonyl-7,9-dimethylbenzopyrromethene hydrobromide 6f (X = Br). Prepared from 3-ethoxycarbonyl-2,4-dimethylpyrrole **5f** and **3b**, dark purple solid, 11%, decomp. 149 °C (DSC) (Found: C, 47.9; H, 3.85; N, 5.8%. $C_{18}H_{18}N_2O_2Br_2$ requires C, 47.6; H, 4.0; N, 6.15%); λ_{max}/nm (ε) 496 (30 800) and 527 (101 000); ν_{max}(KBr)/cm^{-1} 2912 (m), 1688 (m), 1617 (s), 1600 (s), 1279 (s), 1263 (s), 1208 (m), 1110 (m), 1083 (s), 1034 (m) and 756 (m); δ_H(250 MHz) 1.40 (t, *J* 7.1, CH_2CH_3), 2.63, 2.84 (both s, 7- and 9-Me), 4.34 (q, *J* 7.1, CH_2CH_3), 7.53 (s, 5-H), 7.53, 7.72 (both dd, 2^2- and 2^3-H), 7.79 (d, *J* 8.2, 2^1-H), 7.79 (d, *J* 8.2, 2^4-H), 13.15 and 14.20 (both br s, 2 × NH); *m/z* 374 (100, M − HBr), 373 (25) and 372 (96, M − HBr).

1-Bromo-7,8,9-trimethylbenzopyrromethene hydrobromide 6g (X = Br). Prepared from 3,4,5-trimethylpyrrole-2-carboxylic acid **5g** and **3b**, reddish-purple solid, 45%, decomp. 129 °C (DSC) (Found: C, 49.7; H, 4.35; N, 6.95%. $C_{16}H_{15}N_2Br$·0.9HBr requires C, 49.55; H, 4.15; N, 7.2%); λ_{max}/nm (ε) 503 (36 800) and 534 (96 200); ν_{max}(KBr)/cm^{-1} 3019 (m), 2972 (m), 2849 (m), 2672 (m), 1628 (s), 1610 (s), 1555 (m), 1455 (m), 1414 (m), 1273 (s), 1258 (s), 1223 (m), 1155 (m), 1111 (m), 1055 (m), 941 (m), 747 (m) and 682 (m); δ_H(250 MHz) 1.97, 2.33, 2.55 (all s, 3 × Me), 7.40 (s, 5-H), 7.43, 7.61 (both dd, 2^2- and 2^3-H), 7.73 (d, *J* 8.2, 2^1-H), 7.92 (d, *J* 8.5, 2^4-H), 13.34 and 15.18 (both br s, 2 × NH); *m/z* 317 (17), 316 (85, M − HBr), 315 (39) and 314 (90, M − HBr) (Found: M$^+$, 314.0418; calc. for $C_{16}H_{15}N_2Br$, *M*, 314.0419).

opp-Dibenzoporphyrins

2,12-Dimethyldibenzo[*g*,*q*]porphyrin 7a. 1-Chloro-7,9-dimethylbenzopyrromethene hydrobromide **6a** (X = Cl; 79 mg) was heated in *o*-dichlorobenzene (10 ml) at 196 °C for approximately 6 h, the loss of the benzopyrromethene peak being followed by VIS spectroscopy. The cooled mixture was filtered through a pad of Merck Kieselgel 60H, the bed being thoroughly washed with chloroform to remove traces of porphyrin. The filtrate was concentrated and subjected to preparative TLC eluting with toluene–light petroleum (bp 40–60 °C), 7:3. One major porphyrin eluted with R_f *ca.* 0.9; a further quantity of material was obtained on re-chromatographing the base line material, indicative of the low solubility of the product. The total yield of the *title compound* was 2.2 mg (4%), mp > 300 °C (Found: M$^+$, 438.1845. $C_{30}H_{22}N_4$ requires *M*, 438.1844); λ_{max}($CHCl_3$)/nm (rel. A) 387 (0.16), 410 (1.00), 476 (0.02), 539 (0.08), 569 (0.02), 586 (0.02) and 644 (0.06); δ_H(250 MHz, $CDCl_3$) −3.66 (br s, 2 × NH), 3.85 (s, 2 × Me), 8.08–8.11 (complex m, 4 H, 'outer' benzenoid H), 9.22 (br s, 2 H, 2 × β-H), 9.29–9.36 (complex m, 4 H, 'inner' benzenoid H), 10.36, 10.40 (both s, 4 × *meso*-H).

The dibenzoporphyrin **7a** was obtained in similar yield from the bromobenzopyrromethene **6a** (X = Br).

2,12-Diethyl-3,13-dimethyldibenzo[*g*,*q*]porphyrin 7b. (*a*) *From* **6b.**—1-Chloro-7-ethyl-8,9-dimethylbenzopyrromethene hydrobromide **6b** (X = Cl; 44 mg) was heated in *o*-dichlorobenzene (44 ml) at 196 °C for 3 h. Work up gave 16 mg (54%) of the dibenzoporphyrin **7b**, purple crystals, mp > 300 °C, from chloroform (Found: M$^+$, 494.2457. $C_{34}H_{30}N_4$ requires *M*, 494.2470); λ_{max}($CHCl_3$)/nm (ε) 387 (72 000), 410 (523 000), 516 (10 000), 548 (40 100). 585 (7300) and 642 (26 000) [lit.,[13] 387 (79 400), 410 (589 000), 514 (10 000), 548 (43 600), 584 (7400) and 641.5 (29 500)]; δ_H(250 MHz, $CDCl_3$) −3.51 (br s, 2 × NH), 1.95 (t, *J* 7.6, 2 × CH_2CH_3), 3.78 (s, 3-Me and 13-Me), 4.26 (q, *J* 7.6, 2 × CH_2CH_3), 8.01–8.12 (m, 4 H, 'outer' benzenoid H), 9.37–9.40 (m, 4 H, 'inner' benzenoid H), 10.46 (s, 4 × *meso*-H); *m/z* 496 (7%), 495 (39), 494 (100, M) and 247 (18).

(*b*) *From* **6c.**—1-Chloro-8-ethyl-7,9-dimethylbenzopyrromethene hydrobromide **6c** (X = Cl; 40 mg) was treated as above to give purple crystals (8.4 mg, 31%) of the

dibenzoporphyrin **7b**, identical (mixed TLC, ^{1}H NMR, VIS, IR) with the sample from (*a*) above.

2,3,12,13-Tetramethyldibenzo[*g*,*q*]porphyrin 7c. 1-Bromo-7,8,9-trimethylbenzopyrromethene hydrobromide **6g** (X = Br; 107 mg) was heated in *o*-dichlorobenzene (100 ml) at 196 °C for 3 h. The cooled solution was filtered through a pad of silica gel, and the pad was washed copiously with chloroform. The filtrate was concentrated, the precipitate filtered off, washed with chloroform, and dried to give 2,3,12,13-*tetramethyldibenzo*[g,q]*porphyrin* **7c** as a purple–black solid (3.0 mg, 5%) (Found: M^+, 466.2157. $C_{32}H_{26}N_4$ requires *M*, 466.2157). The product had a very low solubility in common organic solvents. λ_{max}(*o*-$C_6H_4Cl_2$, heating to dissolve)/nm (ε) 390 (57 000), 413 (446 000), 518 (7000), 551 (38 900), 586 (6000) and 644 (24 800); ν_{max}(KBr)/cm^{-1} 3330 (m), 1431 (m), 1396 (m), 1320 (m), 1226 (m), 1126 (m), 1088 (s), 1055 (m), 835 (m), 761 (s), 708 (s), 691 (m) and 659 (m); δ_H(250 MHz, $CDCl_3$–CF_3CO_2D) −2.60 (br s, 2 × NH), 3.68 (s, 4 × Me), 8.50–8.54 (m, 4 H, 'outer' benzenoid H), 9.60–9.64 (M, 4 H, 'inner' benzenoid H) and 10.92 (s, 4 × *meso*-H); *m*/*z* 467 (28%), 466 (100, M) and 233 (40).

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