The First Examples of Planar Chiral Organic Benzimidazole Derivatives

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Abstract: The synthesis of a number of novel planar chiral benzimidazoles from [2.2]paracyclophane is reported. The key steps include a Buchwald–Hartwig amination of a sterically demanding triflate and the functionalisation of the C-2 bromide.

Key words: planar chirality, heterocycles, cyclophanes, amination

Substituted benzimidazoles are an important class of heterocyclic compounds that have a broad range of chemical and biological uses. They have shown diverse and significant biological activity as anti-allergic,[1] anti-viral,[2] anti-tumour[3] and anti-ulcerative[4] agents. Their simple elaboration, and the control this imparts on both their steric and electronic properties, has resulted in their widespread use as ligands;[5] additionally benzimidazolium salts have been employed as precursors to *N*-heterocyclic carbene ligands,[6] heterazolium organocatalysts[7] and as precursors to ground-state neutral organic electron donors.[8] Benzimidazoles have also been incorporated into specialist materials.[9]

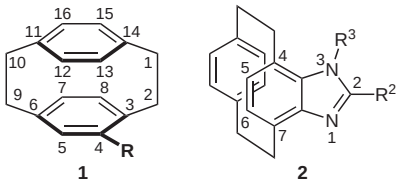

Figure 1

[2.2]Paracyclophane **1** (R = H) and its derivatives are a fascinating family of compounds (Figure 1).[10] Their distinctive structure, comprised of two eclipsing aromatic rings held in place by two ethyl bridges, imparts unique electronic properties and permits the facile formation of planar chiral compounds. These properties have led to [2.2]paracyclophane derivatives being employed in the synthesis of polymers,[11] optoelectronic materials[12] and planar chiral auxiliaries, ligands and catalysts.[13,14] Furthermore, there are a limited number of reports of enantiomerically pure [2.2]paracyclophane derivatives being utilised to probe the effect of planar chirality on stereocontrolled recognition processes in biological systems.[15,16] We have an interest in the synthesis of substituted [2.2]paracyclophanes[17,18] and were attracted to the preparation of a novel class of planar chiral benzimidazole derivatives **2** (Figure 1) based on the [2.2]paracyclophane backbone, as this motif displays great potential for a range of applications. Herein, we present the synthesis and elaboration of the novel planar chiral [2.2](4,7)benzimidazoloparacyclophane moiety **2**.

Our initial goal was to devise a general synthesis of the [2.2](4,7)benzimidazoloparacyclophane **2** moiety. Ideally, the route would be capable of furnishing enantiomerically pure derivatives without recourse to untested resolution steps and the substituents on both C-2 and N-3 (benzimidazole **2** numbering; Figure 1) should be amenable to late-stage modification to allow a range of compounds to be easily accessed. As 4-monosubstituted [2.2]paracyclophane derivatives are readily available in enantiomerically pure form via either our own sulfoxide-based methodology[17] or classical resolution,[13] they offer an ideal starting point for any synthesis. With this caveat in mind it should be noted that all the work carried out in this communication was performed with racemic material.

It is recognised that one of the main problems in the synthesis of disubstituted [2.2]paracyclophane derivatives is the regioselective incorporation of the second substituent. We reasoned that selective introduction of a second amine moiety could be achieved via the directed *ortho*-lithiation of a 4-amino[2.2]paracyclophane derivative. It is known that the directed metallation of [2.2]paracyclophane derivatives can be highly problematic[19,20] and all our studies on amine-based directing groups bore this out; Bräse recently reached a similar conclusion.[21] As a result, a range of *ortho*-directing groups known to work efficiently on [2.2]paracyclophane were investigated. The most promising were the 4-*N*,*N*-diethylcarboxamide[20] and the 4-*N*,*N*-diethylcarbamate groups,[22] which both furnished C-5 functionalised disubstituted derivatives in good yields. Severe problems with the hydrolysis of the amide ultimately led to the use of the carbamate as the directing group.

Having found a suitable directing group, our target became the synthesis of the salicylic acid analogue **5** (Scheme 1). This compound contains suitable functionality for the introduction of both the required nitrogen moieties; the alcohol can be derivatised to allow Buchwald–Hartwig amination,[23] whilst the carboxylic acid can undergo Curtius rearrangement to give N-1. To the best of our knowledge, there are no reports of acid **5**, which is surprising considering its potential. The acid was prepared from 4-bromo[2.2]paracyclophane **3** in four high-yielding

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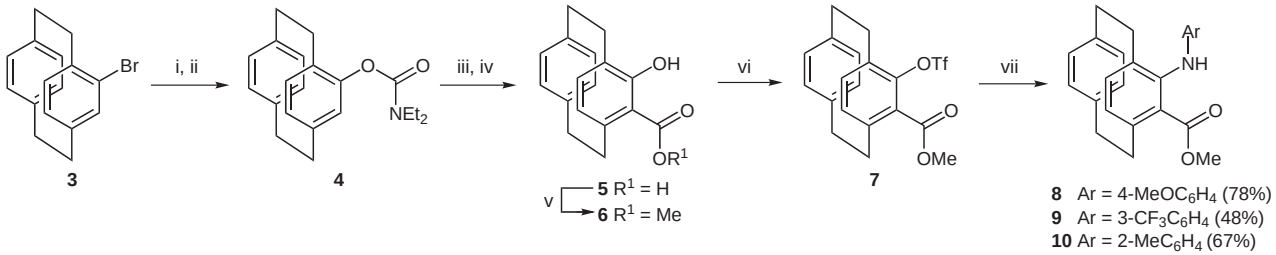
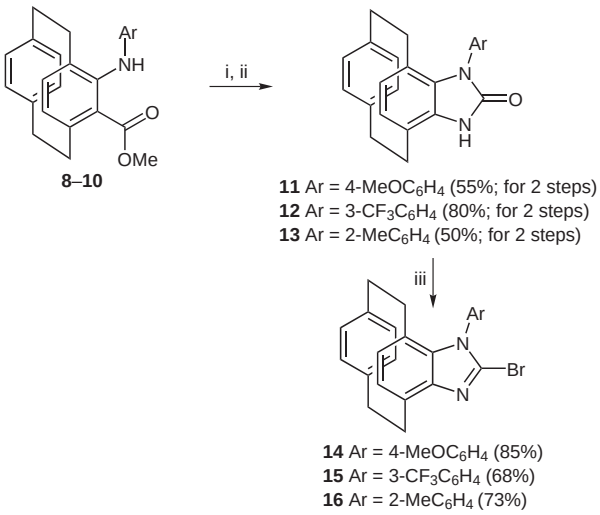


Scheme 1 *Reagents and conditions*: i. a) *n*-BuLi, THF, –78 °C; b) $B(OMe)_3$; c) NMO, reflux. ii. $ClC(O)NEt_2$, DMAP, toluene, 90 °C (65% for two steps); iii. a) *s*-BuLi, TMEDA, THF, –78 °C; b) solid CO_2; iv. 2 M aq HCl, toluene, 90 °C (81% for two steps); v. K_2CO_3, MeI, MeCN (92%); vi. Tf_2O, py, CH_2Cl_2, 0 °C (82%); vii. $Pd_2(dba)_3$ (5%), (±)-BINAP (7.5%), $ArNH_2$, Cs_2CO_3, toluene, reflux, then dropwise addition of **7** in toluene.

steps (Scheme 1). First **3** was converted to 4-hydroxy[2.2]paracyclophane via formation of the boronic ester and in situ oxidation using *N*-methyl morpholine *N*-oxide according to the procedure of Gotteland.[24] The carbamate **4** was then prepared under standard acylation conditions. Finally, directed *ortho*-lithiation with *s*-BuLi and TMEDA followed by reaction with crushed solid CO_2 and subsequent acid hydrolysis gave the acid **5** in good yield. This reaction sequence is amenable to large-scale synthesis of intermediate **5**; we regularly prepare the acid on a 5–10 g scale. It was deemed prudent to install the substituted amine at C-4 ([2.2]paracyclophane numbering or N-3 of benzimidazole **2**) prior to the Curtius rearrangement. To this end the carboxylic acid was protected as the methyl ester **6** and the hydroxyl group was converted to triflate **7** in good yield (Scheme 1).

There were few reports of palladium-mediated coupling reactions of [2.2]paracyclophane-derived triflates[25] and, to our knowledge, only a limited number of palladium-mediated aminations of [2.2]paracyclophane-based compounds.[15,26] At the outset of this project all examples, with the exception of those of Rossen,[27] employed 4-monosubstituted [2.2]paracyclophanes. Recently, Bräse reported one example of the amination of a 4,5-disubstituted derivative analogous to those in this paper (vide infra).[21] In all but the latter example, a strong base, *t*-BuONa, which we considered incompatible with our system, had been utilised. Furthermore, triflate **7** is sterically congested, containing two *ortho* substituents and one face of the aryl system blocked by the lower ring of [2.2]paracyclophane, thus rendering it a challenging example of the Buchwald–Hartwig methodology. Initial attempts at coupling *p*-methoxyaniline, employing the conditions of Buchwald,[28] with Cs_2CO_3 as base and racemic BINAP as ligand, furnished the desired product, **8**, in moderate yield (50%), along with unreacted starting material and considerable quantities of phenol **6**, the result of triflate hydrolysis. This latter side-reaction could be minimised by the slow dropwise addition of a solution of triflate **7** to the reaction mixture already pre-heated to reflux. Under these optimised conditions the yield rose to an excellent 78% on a 10 mmol (4.1g of **7**) scale.[29]

We then evaluated the generality of the amination reaction. The reaction appears to be sensitive to the electronics of the aniline employed; electron-poor *m*-trifluoromethylaniline gave only 48% of **9** under the optimised conditions with competitive hydrolysis of the triflate accounting for the rest of the material. The sterically demanding *o*-toluidine coupled to give the amine **10** in 67% yield. Neither 2,6-diisopropylaniline nor hexylamine furnished the desired amines. In both cases only a mixture of starting material and **6** were isolated. Presumably, the former is too sterically challenging whilst aliphatic amines are notoriously poor coupling partners with *ortho*-substituted arenes.[28]



Scheme 2 *Reagents and conditions*: i. NaOH, H_2O–EtOH, reflux; ii. a) DPPA, Et_3N, toluene, r.t.; b) reflux; iii. $POBr_3$, toluene, reflux.

Having installed one amine unit, we then set about the introduction of the second, which was to be achieved via Curtius rearrangement. Simple base-promoted hydrolysis of the esters followed by an expedient, 'one-pot' modification of the Curtius rearrangement gave an isocyanate that the adjacent aniline attacked to yield the imidazolidinones **11**–**13** (Scheme 2). In order to enable the facile introduction of a range of C-2 (benzimidazole numbering) substituents, we converted the carbonyl moiety to a bromide by treatment with phosphorus(V) oxybromide in toluene at reflux to cleanly give the desired 2-bromo[2.2](4,7)benzimidazoloparacyclophanes **14**–**16** (Scheme 2).[30] The X-ray structure of bromide **14** is shown in Figure 2.[31]

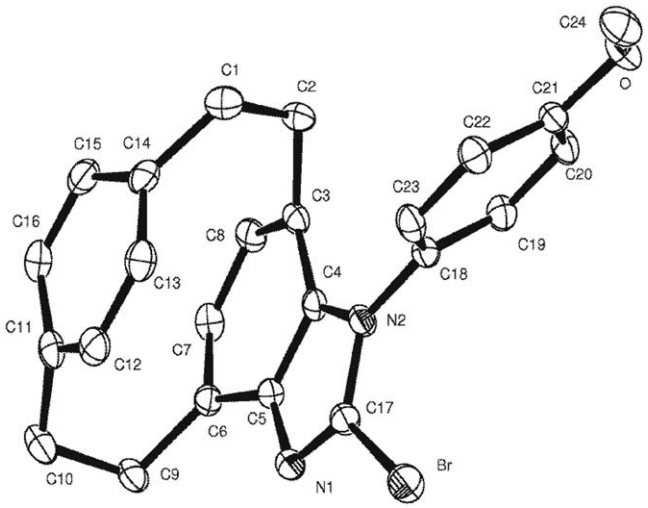
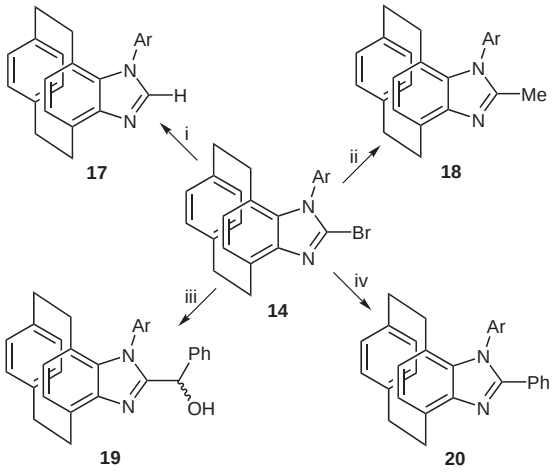


Figure 2 ORTEP representation of molecular structure of 2-bromobenzimidazole **14** in the solid state.



Scheme 3 *Reagents and conditions*: i. a) *n*-BuLi, THF, –78 °C; b) H_2O (89%); ii. a) *n*-BuLi, THF, –78 °C; b) MeI (42%); iii. a) *n*-BuLi, THF, –78 °C; b) PhCHO (61%); iv. $Pd(PPh_3)_4$, K_2CO_3, $PhB(OH)_2$, toluene, reflux (50%). Ar = 4-$MeOC_6H_4$.

The 2-bromobenzimidazole derivative **14** is a versatile intermediate permitting access to a wide range of planar chiral compounds. Scheme 3 gives an initial indication of the possible functionality that can be appended at the 2-position. Treatment with *n*-BuLi furnished the C-2 anion and this was reacted with a range of electrophiles; simple protonation by the addition of water gave the parent benzimidazole derivative **17** in 89% yield. Alkylation with methyl iodide furnished **18** in 42% yield; the main product of this reaction results from protonation. Addition of the anion to benzaldehyde gave rise to a 1:1 mixture of the two possible diastereoisomeric alcohols **19** (61%), with the remainder of the material being **17** again. These are readily separated by column chromatography and the relative stereochemistry was determined by X-ray crystallography (Figure 3).[32] The competence of the bromide **14** in palladium-mediated couplings was evaluated by standard Suzuki–Miyaura reaction with phenylboronic acid catalysed by tetrakis(triphenylphosphine)palladium(0). Under non-optimised conditions, 50% of the desired product **20** was isolated.

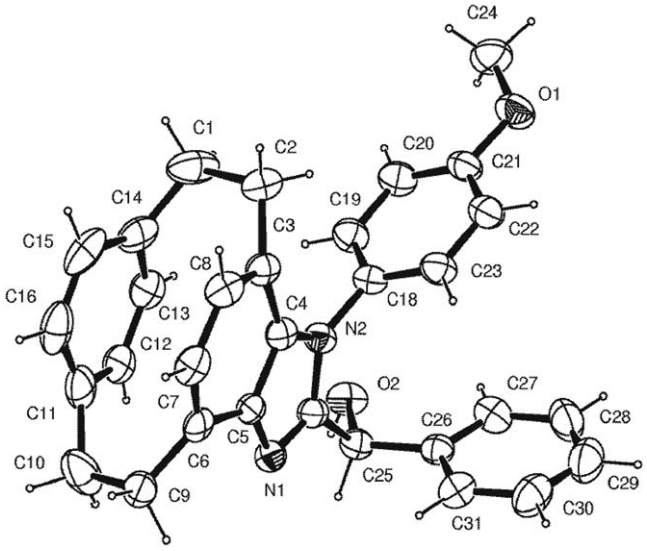


Figure 3 ORTEP representation of molecular structure of one diastereoisomer of alcohol **19** in the solid state.

In conclusion we have devised an efficient synthesis of a series of planar chiral benzimidazole derivatives based on [2.2]paracyclophane. Judicious incorporation of bromide functionality at C-2 permits the facile elaboration of the basic backbone to be achieved at a late stage. Whilst the present chemistry was performed with racemic material, resolution of any one of the intermediates should be readily achievable. We are currently investigating the utility of a number of these compounds in enantioselective catalysis and the results will be reported in due course. Additionally, it should be noted that our route can be readily modified to permit the simple preparation of a number of 4,5-disubstituted [2.2]paracyclophane derivatives, a substitution pattern that is often hard to obtain.

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(29) 4-(4-Methoxyphenylamino)[2.2]paracyclophan-5-yl Carboxylic Acid Methyl Ester (**8**); Typical Procedure: A solution of triflate **7** (4.00 g, 9.66 mmol) in toluene (20 mL) was added dropwise over 1 h to a mixture of *p*-anisidine (1.46 g, 11.59 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.44 g, 0.48 mmol), (±)-BINAP (0.45 g, 0.72 mmol) and Cs_2CO_3 (4.31 g, 13.23 mmol) in toluene (10 mL) at reflux. The mixture was stirred at this temperature for a further 12 h. The reaction was cooled to r.t., filtered through celite and concentrated. The crude product was purified by flash column chromatography (4% Et_2O–PE → 8% Et_2O–PE) to afford **8** as a bright yellow crystalline solid (2.90 g, 78%); mp 174–176 °C. IR ($CHCl_3$): 3336, 2947, 1680, 1574, 1514, 1461, 1439, 1415, 1240 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.61 (1 H, s, NH), 7.04 (1 H, dd, *J* = 7.8, 1.8 Hz, H-15 or H-16), 6.88 (2 H, d, *J* = 8.4 Hz, MeOAr-H), 6.78 (2 H, d, *J* = 8.4 Hz, MeOAr-H), 6.61 (1 H, dd, *J* = 7.8, 1.5 Hz, H-15 or H-16), 6.52–6.45 (3 H, m, H-12, H-13 and H-7 or H-8), 6.39 (1 H, d, *J* = 7.8 Hz, H-7 or H-8), 3.85 (3 H, s, OMe), 3.71 (3 H, s, OMe), 3.63 (1 H, ddd, *J* = 12.6, 9.6, 2.4 Hz, H-9), 3.12 (1 H, ddd, *J* = 12.0, 9.6, 2.1 Hz, H-10), 2.97–2.61 (5 H, m, 5 × CH_2), 2.59–2.45 (1 H, m, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3 (C=O), 154.8 (C), 144.0 (CH), 142.1 (C), 139.9 (C), 139.5 (CH), 138.7 (C), 137.6 (C), 133.5 (C), 133.4 (CH), 132.1 (CH), 130.9 (CH), 129.5 (CH), 127.8 (CH), 121.5 (C), 118.9 (CH), 114.8 (CH), 56.1 (CH_3), 52.2 (CH_3), 36.6 (CH_2), 35.3 (CH_2), 35.3 (CH_2), 34.3 (CH_2). MS (EI): *m*/*z* = 387 $[M]^+$, 355, 354 $[M - CH_3OH]^+$, 283, 268, 251, 236, 220, 208, 192. HRMS (EI): *m*/*z* calcd for $C_{25}H_{25}NO_3$ (MH^+): 388.1907; found: 388.1905.
(30) 2-Bromo-3-(4-methoxyphenylamino)[2.2](4,7)benzimidazoloparacyclophane (**14**); Typical Procedure: A solution of **11** (0.41 g, 1.12 mmol) and phosphorus(V) oxybromide (0.80 g, 2.80 mmol) in toluene (16 mL) was heated to reflux for 5 h. The reaction mixture was cooled to r.t. and washed with a sat. aq soln of $NaHCO_3$ (25 mL). The organic layer was separated and the aq layer extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts were filtered to remove any insoluble impurities, dried ($MgSO_4$), concentrated and purified by flash column chromatography (10% heptane–Et_2O→ 20% heptane–Et_2O) to afford **14** as a white crystalline solid (0.41 g, 85%); mp 156–159 °C. IR ($CHCl_3$): 3010, 2959, 2932, 2954, 1609, 1585, 1511, 1456, 1300, 1253, 1169 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.65 (1 H, dd, *J* = 8.7, 2.4 Hz, H-2 or H-6 of $MeOC_6H_4$), 7.08 (1 H, dd, *J* = 8.7, 2.7 Hz, H-2 or H-6 of $MeOC_6H_4$), 7.02 (1 H, dd, *J* = 8.7, 2.4 Hz, H-3 or H-4 of $MeOC_6H_4$), 6.90 (1 H, dd, *J* = 8.7, 3.0 Hz, H-3 or H-4 of $MeOC_6H_4$), 6.51 (1 H, d, *J* = 7.5 Hz, H-5 or H-6), 6.39–6.41 (2 H, m, H-5 or H-6 and pseudo-*p* N-1 or pseudo-*p* N-3), 6.28 (1 H, dd, *J* = 7.8, 1.5 Hz, pseudo-*p* N-1 or pseudo-*p* N-3), 6.22 (1 H, dd, *J* = 7.8, 1.8 Hz, pseudo-*gem* N-1 or pseudo-*gem* N-3), 6.05 (1 H, dd, *J* = 7.8, 1.8 Hz, pseudo-*gem* N-1 or pseudo-*gem* N-3), 3.84 (3 H, s, OMe), 3.67–3.75 [1 H, m, (C-7)-CH_2], 3.03 [1 H, ddd, *J* = 14.4, 12.3, 4.2 Hz, (C-7)-CH_2CH_2], 2.96–2.71 (2 H, m, CH_2), 2.53–2.37 (1 H, m, CH_2), 2.11 [1 H, ddd, *J* = 12.9, 9.6, 7.2 Hz, (C-4)-CH_2]. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.3 (C), 145.4 (C), 139.3 (C), 138.1 (C), 138.0 (C), 133.0 (CH), 132.0 (C), 131.8 (CH), 131.3 (CH), 129.7 (C), 129.6 (C), 129.5 (CH), 129.3 (C), 129.0 (CH), 128.7 (CH), 127.1 (CH), 125.4 (CH), 125.1 (C), 115.1 (CH), 114.7 (CH), 56.1 (CH_3), 35.4 (CH_2), 34.9 (CH_2), 31.9 (CH_2), 30.8 (CH_2). MS (EI): *m*/*z* = 435 $[^{81}M]^+$, 433 $[^{79}M]^+$, 330, 328, 297, 299, 249, 205. HRMS (EI): *m*/*z* calcd for $C_{24}H_{21}N_2OBr$ ($^{79}MH^+$): 433.0910; found: 433.0903.
(31) CCDC 611020 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts.retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (1223)336033; e-mail: deposit@ccdc.cam.ac.uk].
(32) CCDC 611019 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts.retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (1223)336033; e-mail: deposit@ccdc.cam.ac.uk].