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The synthesis of the first chiral superstructured corrole has been achieved by reacting an original bis(diaminophenyl)-corrole with two chiral binaphthyl bis(acid chloride) handles.

Introduction

During the last few decades, the chemistry of porphyrins has received considerable attention, and as a result, tremendous strides have been made in the development of new synthetic methods to prepare these materials. Undoubtedly, these ongoing efforts can be attributed to the remarkable properties of the porphyrin core that allow its use in areas as disparate as catalysis, biomimetic modelling, medicinal chemistry and materials.¹ Perhaps due to their relatively facile synthesis, porphyrins (and porphyrinogens) have long remained the only tetrapyrrolic macrocycle widely studied. However, more recently, a number of different groups have dedicated their efforts towards the preparation of “contracted” or “expanded” porphyrins, their goal being to investigate and compare the properties of these materials with the parent porphyrin.² Amongst these systems, it could be argued that corrole has received most attention.

For many years, the investigation of the interesting features of the corrole core was hampered by the limited synthetic availability of this macrocycle. This situation changed in 1999 when a number of groups independently reported the improved syntheses of triarylcorroles. In particular, Gross *et al.* first reported an 11% yield, solvent-free synthesis of tris(pentafluorophenyl)-corrole by mixing the highly reactive pentafluorobenzaldehyde and pyrrole.³ In parallel, Paolesse *et al.* described the synthesis of the regular triphenylcorrole in an unoptimized 6% yield using a modified Rothmund synthesis.^{4,5}

Other corrole syntheses involving stepwise reactions have also been proposed. Of these, some require the preparation of di- or tripyrromethanes. The latter precursors can afford the expected corroles upon final oxidative cyclization in reasonable yields. However, certain drawbacks inherent to the use of large excesses of dipyrromethanes, or limitations concerning the nature of the aldehyde narrow the convenience of the method.⁶⁻⁹ In particular, to the best of our knowledge, there are no reports concerning the use of sterically crowded 2,6-dinitrobenzaldehydes as corrole precursors. Here, we wish to report the synthesis of a new tetranitrocorrole in addition to the condensation of chiral handles with the corresponding reduced tetraaminocorrole.

Results and discussion

For many years our group has considered that corrole chemistry is an essential complement to porphyrin chemistry. A number of years ago, we unexpectedly isolated the tris(2,6-dinitro-4-*tert*-butylphenyl)corrole **1** as a minor by-product in a classical porphyrin synthesis (Fig. 1).¹⁰ We have recently re-investigated its synthesis.

A modified Rothmund synthesis⁴ involving 2,6-dinitro-4-*tert*-butylbenzaldehyde¹⁰ **2** and pyrrole did not afford the

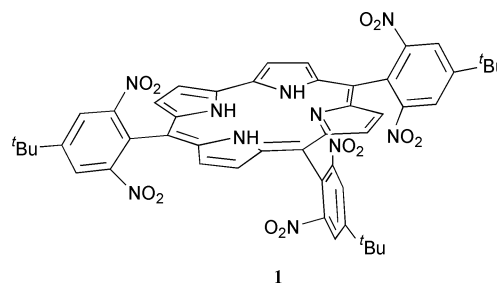
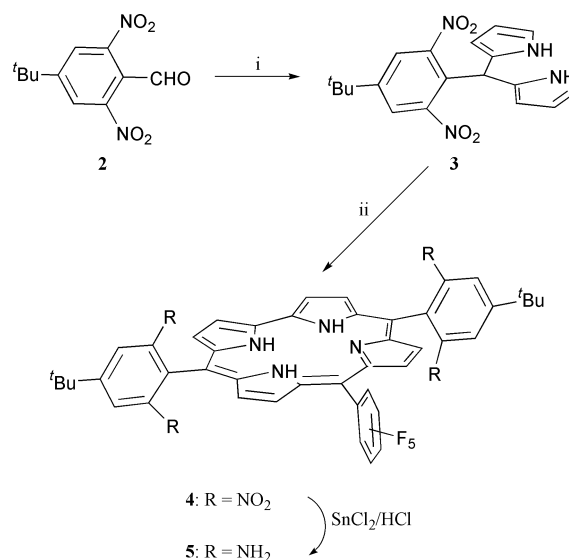


Fig. 1 5,10,15-Tris(2,6-dinitro-4-*tert*-butylphenyl)corrole **1**.

expected corrole. The solvent free approach³ appeared not to be successful either, even in the presence of a catalyst. Consequently, we prepared the new 5-(2,6-dinitro-4-*tert*-butylphenyl)dipyrromethane **3** in 70% yield after chromatographic purification, according to usual procedures.¹¹ Unfortunately, despite many changes in the reaction conditions, condensation of **2** with **3** did not afford the expected corrole **1**.

In order to test the influence of the nature of the aldehyde, we decided to react **3** with pentafluorobenzaldehyde. We chose pentafluorobenzaldehyde because firstly we needed a reactive, electron poor aldehyde and secondly, we wished to prepare A₂B-corroles that have suitable topography for the preparation of C₂-symmetrically elaborated systems. Condensation of pentafluorobenzaldehyde with **3** in the presence of BF₃·OEt₂ followed by *in situ* oxidative coupling with 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) afforded the expected bis(dinitrophenyl)corrole **4** in an unexpected 24% yield without any trace of porphyrin (Scheme 1).[†]

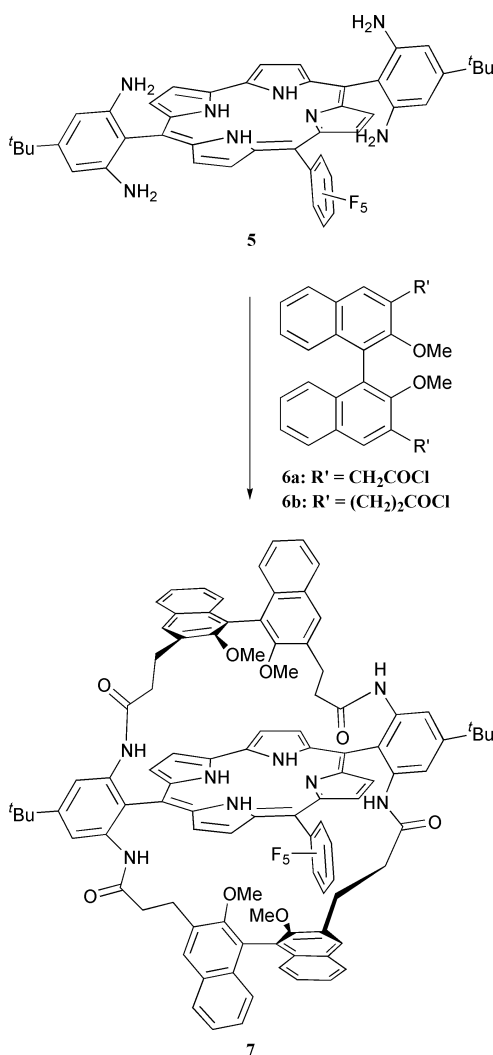
Thus, the reduced reactivity of **2** with respect to pentafluorobenzaldehyde along with an increased steric hindrance explains the unsuccessful preparation of **1**.⁸



Scheme 1 Reagents: i, excess pyrrole, BF₃·OEt₂; ii, 0.5 eq. C₆F₅CHO, BF₃·OEt₂, NH₄Cl, propionitrile.

Corrole **4** was further reduced to the corresponding tetra-aminocorrole **5** using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in acidic medium in 80% yield. We then decided to use **5** as a precursor to prepare new binaphthyl-strapped chiral corroles. In our previous investigations we have shown that porphyrinoid systems can be remarkably efficient for the epoxidation of non-activated terminal olefins¹² and we therefore decided to investigate the activity of these corrole systems in similar reactions. Previously, we described the preparation of binaphthyl-strapped porphyrins¹² by condensing the binaphthyl bis(acid chloride) **6a**¹³ and the $\alpha^2\beta^2$ atropisomer of tetrakis(2-aminophenyl)porphyrin.¹⁴ Unfortunately, a CPK model revealed that the latter strap is too short for the optimized synthesis of a binaphthyl-corrole. Thus, we developed a preparation of a new "homologated" binaphthyl bis(acid chloride) **6b** the synthesis of which will not be described in this communication.

High dilution condensation of two equivalents of **6b** with **5** afforded the first example of chiral strapped corrole **7** in 25% yield (Scheme 2).[‡]



Scheme 2 Reagents and conditions: high dilution, THF, *N,N*-diethylaniline.

Conclusions

In conclusion, we have shown that the preparation of highly functionalized corroles, namely bis(dinitro-) and bis(diamino-

phenyl)corroles **4** and **5**, are now possible starting from 2,6-dinitro-4-*tert*-butylbenzaldehyde. Trapping the amino functions by a binaphthyl bis(acid chloride) led to the unique superstructured chiral corrole. The structural similarity of compound **7** to a gyroscope has led us to describe this material as "gyroscope-corrole". This represents the first report of a double-faced protected chiral corrole. Further studies concerning the catalytic properties of this material, e.g. asymmetric epoxidation and hydroxylation, are currently under investigation in our laboratory.

Notes and references

† Typical experimental procedure: A 100 cm³ round bottom flask was charged with 5-(2,6-dinitrophenyl-4-*tert*-butyl)dipyrrromethane (500 mg, 1.36 mmol) and 10 cm³ of reagent grade propionitrile. The resulting brown solution was then degassed with N₂ for 15 min before pentafluorobenzaldehyde (133 mg, 0.68 mmol) and NH₄Cl (727 mg, 13.6 mmol) were added. Finally, BF₃·Et₂O (16 mm³, 0.13 mmol) was added with a syringe and the reaction was allowed to proceed at room temperature for 90 min. After the reaction was complete, DDQ (1.36 mmol, 309 mg) was added and the reaction mixture allowed to stir for another 15 min. The crude reaction mixture was then poured onto a pad of 60 μm silica gel and eluted with CH₂Cl₂ and CH₂Cl₂-MeOH 98:2 until no green solution was eluted. The corrole containing solutions were then collected together, evaporated to dryness and purified by chromatography on a basic alumina column with CH₂Cl₂-petroleum ether 1:1 as eluent. Analytically pure compound (150 mg, 24%) was obtained from crystallization (CH₂Cl₂-petroleum ether). ¹H NMR δ_H (200 MHz, CDCl₃) 1.63 (s, 18H, *t*Bu), 8.40–8.43 (s + broad m, 8H, H_{ar} + H_{βpyr}), 8.58 (d, 2H, *J* 4.4, H_{βpyr}), 8.94 (d, 2H, *J* 4.0, H_{βpyr}); HRMS (Maldi-ToF) [Found: (M + H)⁺, 909.1984. C₄₅H₃₃F₅N₈O₈ + H⁺ requires *M*, 909.2420].

‡ Selected data for **7**: ¹H NMR δ_H (500 MHz, CDCl₃) 8.90 (d, 2H, *J* 4.5, H_{βpyr}), 8.79 (d, 2H, *J* 4.5, H_{βpyr}), 8.57 (broad s, 4H, H_{meso-aryl}), 8.43 (d, 2H, *J* 4.4, H_{βpyr}), 8.30 (d, 2H, *J* 4.5, H_{βpyr}), 7.96 (d, *J* 7.8, 2H), 7.84 (broad t, 2H), 7.63 (s, 2H), 7.57 (d, *J* 8.3, 2H), 7.38, (s, 2H), 7.15 (t, *J* 7.8, 2H), 7.08 (t, *J* 8.0, 2H), 6.82 (t, *J* 7.8, 2H), 6.61 (s, 2H), 6.39 (s, 2H), 6.07 (d, *J* 8.7, 2H), 5.72 (d, *J* 8.4, 2H), 3.36 (m, CH₂, 8H), 2.28 (s, 6H, OMe), 1.61 (s, 9H, *t*Bu), 1.53 (s, 9H, *t*Bu), -0.83 (s, 6H, OMe); *m/z* (Maldi-ToF): 1576.87 (M)⁺. UV-Vis absorptions. λ_{max} (CH₂Cl₂)/nm 411, 563, and 598.

- For a complete overview, see for instance, *The Porphyrin Handbook*, ed. K. Kadish, K. M. Smith and R. Guilard, Academic Press, New York, 2000.
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