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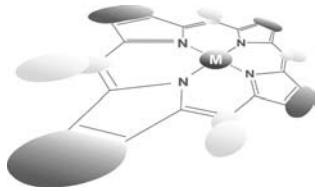

β-octabromo-*meso*-tris(pentafluorophenyl)corrole: reductive demetalation-based synthesis of a heretofore inaccessible, perhalogenated free-base corrole

Can Capar[a], Lars-Kristian Hansen[a], Jeanet Conradie[a,b] and Abhik Ghosh*[a◊]

[a] *Department of Chemistry and Center for Theoretical and Computational, University of Tromsø, N-9037 Tromsø, Norway*
[b] *Department of Chemistry, University of the Free State, Bloemfontein 9300, Republic of South Africa*

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ABSTRACT: Long known in various metal-complexed forms, β-octabromo-*meso*-tris(pentafluorophenyl)corrole, $H_3[Br_8TPFPC]$, has not been available as a free ligand until now. It can be prepared in high yield (86%) *via* reductive demetalation (conc. H_2SO_4, $FeCl_2$) of $Mn[Br_8TPFPC]$. Interestingly, the same conditions did not result in demetalation of the analogous copper complex, which may be contrasted to the behavior of many other copper corroles, which demetalate cleanly. X-ray crystallographic analysis revealed a unique "half-saddled" conformation, wherein two of the pyrrole rings on one side of the direct pyrrole-pyrrole linkage are strongly tilted up and down relative to each other, whereas the other two pyrrole rings are roughly in the mean plane of the macrocycle.

KEYWORDS: demetalation, free-base corrole.

INTRODUCTION

Although the chemistry of corroles has grown spectacularly over the last decade [1–3], the field has long been hobbled by the lack of suitable methods for demetalation of metalocorroles [4, 5], whereby new functionalized free-base corroles might have been accessed. The last couple of years, however, have seen multiple reports of potential solutions to this problem. In the first such report, Paolesse and co-workers reported copper-corrole demetalation with $CHCl_3/H_2SO_4$ [6]. In our own studies on copper corroles [7], we also found concentrated H_2SO_4 to be the acid of choice, albeit with a crucial twist: concentrated H_2SO_4 with several equivalents of a reducing agent such as $FeCl_2$ resulted in dramatically better yields of free-base corrole, fewer impurities, as well as somewhat shorter reaction times, compared to H_2SO_4 alone. Soon thereafter, Dehaen and co-workers reported a similar reductive procedure for copper corroles, involving $SnCl_2$ and concentrated HCl [8], while Chang and co-workers reported that $SnCl_2$/HCl also demetalated manganese corroles [9]. Subsequently, Kadish, Smith, Paolesse and co-workers reported a suite of procedures for the demetalation of silver corroles [10].

Unfortunately, none of the above methods is truly general. For example, when demetalating certain copper β-octabromocorroles, Dehaen *et al.* reported problems with partial debromination of the macrocycle. Although we did not encounter this problem to a significant extent and successfully synthesized free-base β-octabromo-*meso*-triarylcorrole from the corresponding copper complex in reasonably good yield, our procedure did not work satisfactorily for certain other β-octabromocorroles, most notably free-base β-octabromo-*meso*-tris(pentafluorophenyl) corrole, $H_3[Br_8TPFPC]$. Though well-known in metal-complexed form [11], this corrole is unknown as a free-base, a somewhat unfortunate situation, considering that it is a unique perhalogenated, highly electron-deficient ligand whose coordination chemistry and applications deserve to be more fully explored. Here, we report an optimized synthesis of this free-base ligand.

The $H_3[Br_8TPFPC]$ lent itself to crystallization and X-ray crystallographic analysis, although the poor

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*Correspondence to: Abhik Ghosh, email: abhik.ghosh@uit.no

quality of the crystals resulted in a rather imprecise structure. The structure is nonetheless unique [12] and, in light of the relative rarity of such structures, worth describing.

EXPERIMENTAL

Instrumentation

Ultraviolet-visible spectra were recorded on an HP 8453 spectrophotometer with dichloromethane as solvent. NMR spectra were recorded on a Mercury Plus Varian spectrometer (400 MHz for ^{1}H and 376 MHz for ^{19}F) at room temperature in chloroform-*d.* Proton chemical shifts (δ) were referenced to residual chloroform (δ = 7.2 ppm) and ^{19}F chemical shifts (δ) were referenced to 2,2,2-trifluoroethanol-d_3 (δ = -77.8 ppm). MALDI-TOF mass spectra were recorded on a Waters Micromass MALDI micro MX Mass Spectrometer with α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix.

Materials

All reagents and solvents were used as purchased, except pyrrole, which was pre-dried and distilled from CaH_2 at low pressure. Silica gel 60 (0.040–0.063 mm particle size; 230–400 mesh; Merck) was used for flash chromatography. 5,10,15-tris(pentafluorophenyl)corrole, H_3[TPFPC] [12], Mn[TPFPC] [13], and Mn[Br_8TPFPC] [11a] were synthesized according to literature procedures.

Demetalation of Mn[Br_8TPFPC]

Into a 25 mL round-bottomed flask were added 40 mg (0.027 mmol) of Mn[Br_8TPFPC] and 5 equiv. of anhydrous $FeCl_2$ (Sigma-Aldrich) (17.1 mg, 0.135 mmol). Concentrated H_2SO_4 (95–97%, Merck) (3 mL) was added and the mixture was stirred at 40 °C. The progress of the reaction was monitored by UV-vis spectroscopy and by TLC. After 2 h, the reaction mixture was cooled to room temperature and poured into distilled H_2O (300 mL), and then extracted with CH_2Cl_2. The green organic phase was washed twice with distilled water and then twice with saturated aqueous $NaHCO_3$. The organic phase was dried with anhydrous Na_2SO_4, filtered and rotary-evaporated to dryness. The residue was chromatographed on a silica gel column with 1:1 *n*-hexane/CH_2Cl_2. After removal of the solvent, the green product was crystallized from CH_2Cl_2/*n*-hexane to afford 33.2 mg (0.0232 mmol) of the pure free-base. Yield: 86%. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε, $M^{-1}.cm^{-1}$) 444 (5.17), 590 (4.38), 626 (4.17), 671 (3.13). ^{1}H NMR ($CDCl_3$): δ, ppm 2.1 (broad singlet, N*H*). ^{19}F NMR ($CDCl_3$, assigned with ^{19}F-^{19}F COSY): δ, ppm -137.76 (dd, *J* = 26.32 Hz, 7.52 Hz; 2F, 10-*o*-F), -138.60 (d, *J* = 17.30 Hz; 4F, 5,15-*o*-F), -150.69 (t, *J* = 22.56 Hz; 2F, 5,15-*p*-F), -150.91 (t, *J* = 18.80 Hz; 1F, 10-*p*-F), -162.19 (trip-doublet, *J* = 18.80 Hz, 7.52 Hz; 4F, 5,15-*m*-F), -162.79 (trip-doublet, *J* = 26.32 Hz,11.28 Hz; 2F, 10-*m*-F). MS (MALDI-TOF, major isotopomer): *m/z* $[M]^+$ 1427.68 (expt.), 1427.65 (calcd.).

For X-ray analysis, H_3[Br_8TPFPC] was recrystallized from CH_2Cl_2/*n*-hexane solution by slow evaporation. A dark-red prismatic crystal with approximate dimensions 0.25 mm × 0.20 mm × 0.10 mm was mounted on a glass fiber. All measurements were made at room temperature with a Rigaku AFC Kappa four-circle diffractometer and a Rigaku Saturn CCD area detector, using graphite monochromated Mo Kα radiation. The structure was solved by direct methods using SHELX97. Some non-hydrogen atoms were refined anisotropically and the rest isotropically.

The molecule crystallizes in a C-centered monoclinic cell with dimensions: a = 22.306(6) Å, b = 21.147(6) Å, β = 96.585(6)º, c = 18.282(5) Å, V = 8567(4) Å^3. The pace group was determined to be C2/c.

RESULTS AND DISCUSSION

None of the above protocols were successful in demetalating Cu[Br_8TPFPC]. The conditions employed by Dehaen *et al.* (CH_2Cl_2/CH_3CN, $SnCl_2$, HCl) were tried for Cu[Br_8TPFPC], but no free-base could be isolated. However, with our own reductive demetalation method (conc. H_2SO_4, $FeCl_2$), Mn[Br_8TPFPC] was smoothly demetalated in about 50% yield. Optimizing the temperature improved the yield further, up to 86%. Crystals suitable for X-ray analysis, albeit of rather poor quality, could be obtained from CH_2Cl_2/*n*-hexane. Unfortunately, a variety of attempts to obtain crystals of better quality failed.

The key feature of the crystal structure is the conformation of the corrole macrocycle (Fig. 1). It is severely non-planar, but the nature of the non-planar distortion is most unusual. Two of the pyrrole rings are severely tilted, in opposite directions, relative to the mean plane of the corrole, while the other two pyrrole rings are roughly within the mean of the macrocycle plane. To our knowledge, this is an unprecedented [14] conformation for a corrole (or for that matter, for a porphyrin), which may be described as half-saddled in the sense that only half the macrocycle is strongly out-of-plane, relative to a normal saddled porphyrinoid. The C-Br distances vary from 1.86(2) to 1.902(19) Å, with a mean value of 1.88(2) Å. The 15 C-F distances vary from 1.30(3) to 1.40(3) Å, with

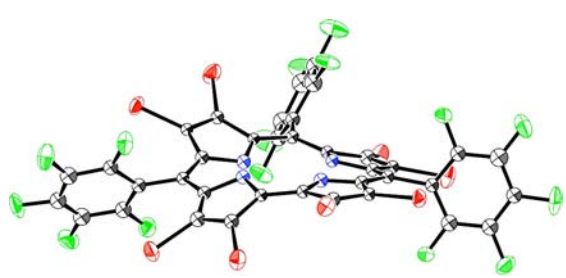

Fig. 1. ORTEP of H_3[Br_8TPFPC]

a mean value of 1.33(3) Å. Due to the difficulty of finding a crystal of good quality, only the F and Br atoms were refined anisotropically, while the C and N atoms were refined isotropically. This was done to keep the reflection/parameter ratio reasonably high. The presence of 8 Br atoms in the molecule, combined with the modest data quality, meant that we were not able to locate the central hydrogen atoms.

To gain deeper insight into the unique structure, we resorted to dispersion-corrected DFT (BP86-D/STO-TZP [15, 16]) calculations. The use of Grimme's [17] empirical corrections for dispersion effects led to significantly lower RMSDs between the optimized and experimental structures, relative to regular dispersion-uncorrected DFT, which should not be surprising given the sterically hindered nature of the molecule. Geometry optimizations were carried out for different arrangements of central protons and two of the resulting structures, shown in Fig. 2, exhibit nearly equally low RMSDs relative to the X-ray structure. Moreover, the two structures, which are different tautomeric forms of the free-base corrole, are equi-energetic to within about 0.01 eV. Thus,

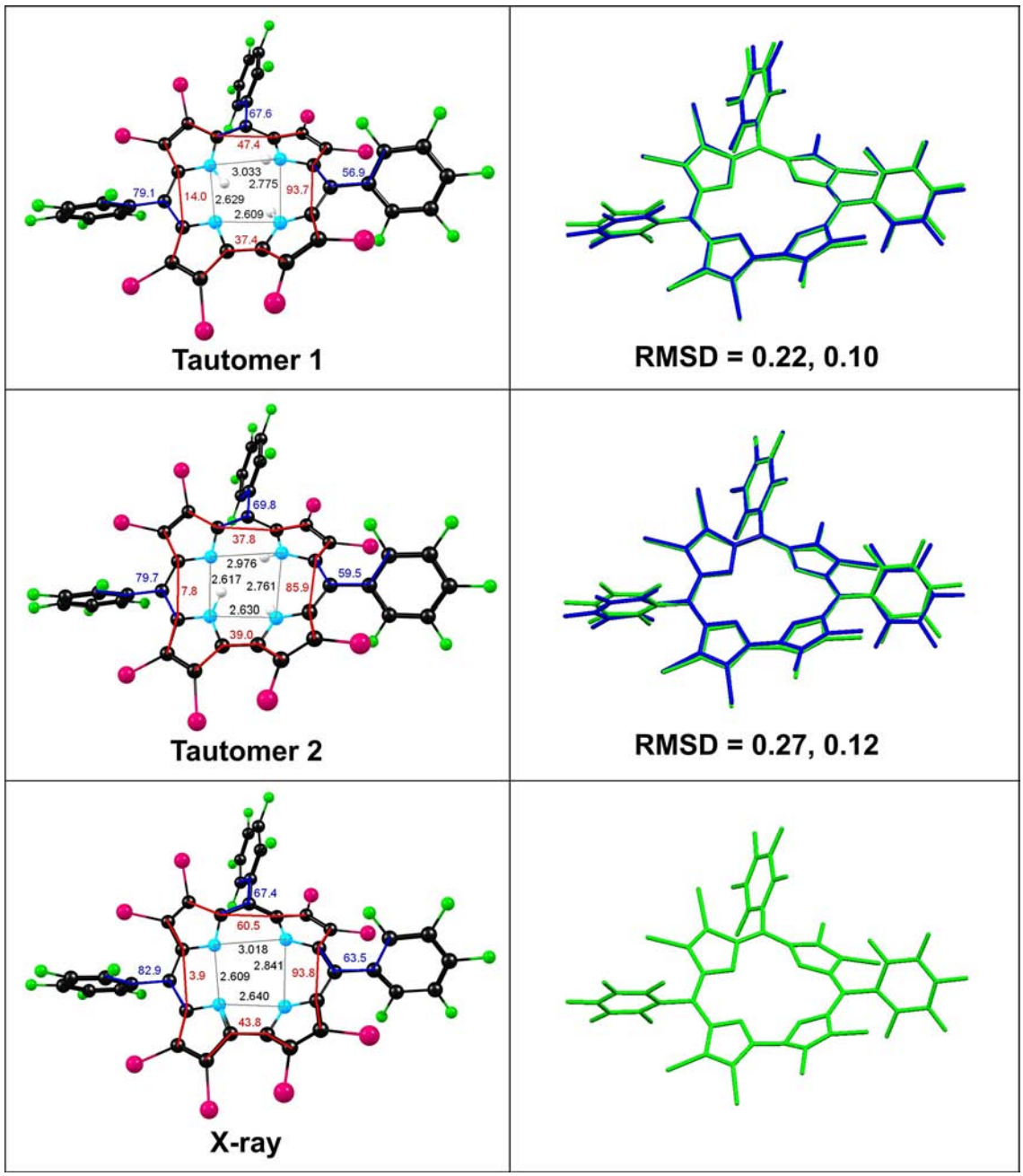

Fig. 2. Highlights of BP86-D optimized geometries (Å, deg) of $H_3[Br_8TPFPC]$ tautomers. Distances are shown in black, corrole saddling dihedrals in red and corrole-aryl dihedrals in blue. Two RMSDs (Å) are indicated for the best overlays of the optimized (blue) and experimental (green) structures; the first including all non-hydrogen atoms, the second excluding the C_6F_5 groups. Metrical parameters for the X-ray structure are shown for comparison

we cannot assign the experimentally observed structure to one tautomeric form or the other, based on our calculations. Indeed, it is entirely possible that both tautomers are present in the crystal.

The DFT calculations nicely reproduce the half-saddled conformation observed in the X-ray structure, suggesting that this unique structure indeed corresponds to the preferred conformation of the free molecule. An examination of the saddling dihedrals (marked in red in Fig. 2) strongly suggests that the non-planarity is *driven* by steric interactions among the three central hydrogens, and is further *enhanced* by the steric crowding on the corrole periphery. The structural literature on corroles, though limited, strongly suggests that peripheral crowding alone often is not sufficient to bring about significant non-planar distortion. Thus, unlike the free-base structure reported here, Co[Br_8TPC](PPh_3) [18] and Ir[Br_8TPFPC](PPh_3) [11c] feature essentially planar macrocycles. Copper corroles, however, are inherently saddled, even if they are sterically unhindered, but the non-planarity in copper case is most likely driven by a specific Cu(d)-corrole(π) orbital interaction [19].

Overall, the main contribution of this study is the synthesis (86% yield) of a heretofore inaccessible free ligand, a perhalogenated free-base corrole. We look forward to using this ligand to synthesize novel complexes that are unlikely to be accessible by other means. Our hope is that the steric features of the Br_8TPFPC ligand will result in novel coordination stereochemistry and reactivity, relative to what has been observed to date with β-unsubstituted ligands.

Supporting information

Crystallographic data for H_3[Br_8TPFPC] have been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition number 767455. Copies can be obtained on request, free-of-charge, *via* www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

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