Oxidized forms of a tripyrrane: α-tripyrrinone, β-tripyrrinone and a C_2 symmetric hexapyrrole†

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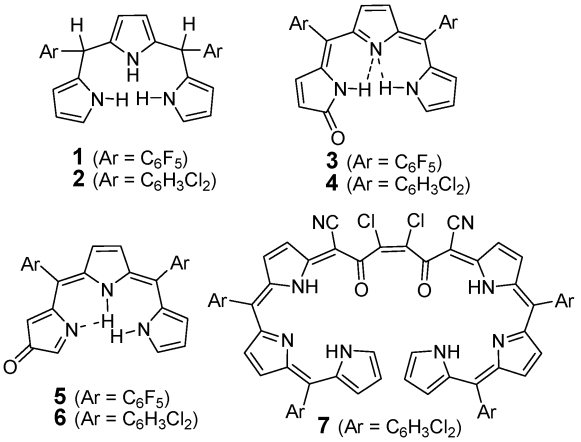
α- and β-tripyrrinone isomers (3–6), and a C_2 symmetric hexapyrrole (7) were isolated from the oxidation of *meso*-perfluorophenyl tripyrrane 1 (and *meso*-2,6-dichlorophenyl tripyrrane 2) with DDQ under aerobic conditions, and the structure of 3 was determined by X-ray crystallographic analysis.

Porphyrins and larger related macrocycles, particularly expanded porphyrins, have been widely studied since these molecules have shown unique chemical and physical properties.[1] Included in the continuing efforts to prepare these macrocycles has been the exploration of improved or new reaction conditions.[2,3] Recently, Osuka *et al.* reported that acid-catalyzed conjugation followed by oxidation, under anaerobic conditions, of a CH_2Cl_2 solution of a *meso*-perfluorophenyl substituted tripyrrane under refluxing conditions formed a rubyrin and a nonaphyrin (1.1.0.1.1.0.1.1.0).[4] Our recent research on DDQ-oxidation of tripyrranes under aerobic conditions resulted in the formation of the tripyrrinone compounds **3–6** and a DDQ adduct,‡ the tripyrrin dimer **7**. The structure of tripyrrinone **3** was determined by X-ray crystallography (Fig. 1).§



When tripyrrane **1** was briefly oxidized by DDQ under aerobic conditions tripyrranone **3** and its isomer **5** were formed. The X-ray crystallographic data of **3** describes a structure having intermolecular N–H···N hydrogen-bonds (Fig. 1). The interior C–N–C angles on each pyrrole unit reveal both amino-type (111.4° for C(1)–N(1)–C(4) and 110.7° for C(11)–N(3)–C(14)) and imino-type nitrogen atoms (105.1° for C(6)–N(2)–C(9)). As a result of the steric hindrance between the hydrogens on N(1) and N(3), the mean plane of the tripyrrinone is slightly twisted (the dihedral angle between the dipyrrolyl plane containing the N(1) and N(2) atoms and the pyrrole plane containing the N(3) atom is 25.8°). Each amino-H atom forms hydrogen-bonds with an imino-N atom [bond lengths(Å): 2.19; 2.25].

The ^{1}H NMR spectrum of **3** in CD_2Cl_2 shows downfield shifts for the two amino-H peaks resulting from hydrogen-bonding effects (Fig. 2(a)). Two broad singlets at 11.58 and 10.01 ppm were assigned to the amino-Hs. In comparison to compound **3**, the ^{1}H NMR spectrum of **5** showed two broad singlets for the amino-H atoms with significantly different chemical shifts of 12.03 and 8.00 ppm (Fig. 2(b)). This results from the greater distance between the amino-Hs for this compound preventing the formation of intramolecular hydrogen-bonds. Two sets of doublets (a set at 6.85 and 6.35 ppm and the other set at 6.75 and 6.28 ppm, see Fig. 3(a)) in the spectrum of **3** were assigned to the peaks of the two pyrrole units having substituted α-positions and the peaks at 7.51 and 6.43 ppm were assigned as the peaks for the α and β-Hs on the terminal pyrroles having unsubstituted α-positions. These sets of peaks are distinguishable from those of **5** which resonate over a relatively wider range between

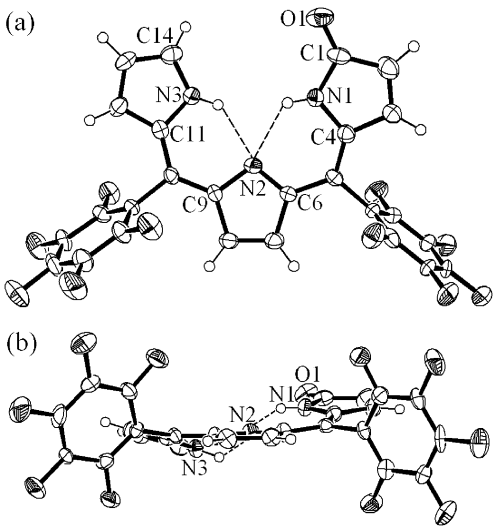


Fig. 1 Crystal structure of **3**; the dashed line indicates the intramolecular hydrogen-bonds: (a) top view and (b) side view. Thermal ellipsoids are scaled to the 50% probability level.

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† Electronic supplementary information (ESI) available: Experimental and spectral data for compounds **3** and **7**, crystallographic data for compound **3** and the structural proof for compounds **3** (CIF) and **7**. CCDC 693823. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901171b

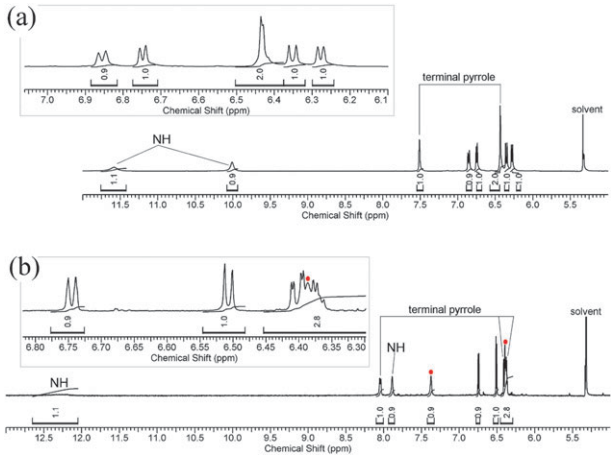

Fig. 2 ^{1}H NMR spectra of **3** (a) and **5** (b) in CD_2Cl_2.

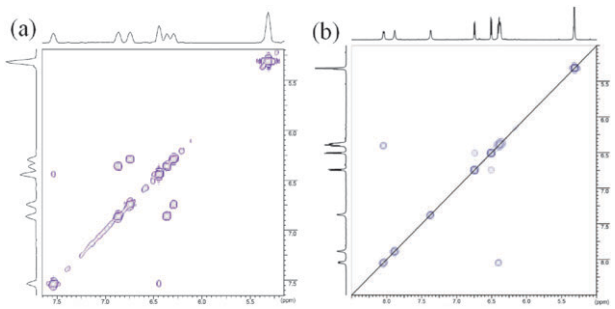

Fig. 3 HHCOSY spectra of **3** (a) and **5** (b) in CD_2Cl_2 after adding D_2O.

8.1 and 6.5 ppm, in the absence of hydrogen-bonding (Fig. 3(b)). The α- and β-Hs on the oxo-pyrrole of **5** were observed as singlets at 7.35 and 6.39 ppm (red dots in Fig. 2(b)). As a result of the oxo-group at the β-position direct coupling between the α-H and the remaining β-H was not detected in the HHCOSY NMR spectrum (Fig. 3(b)). Correspondingly, differences in the two isomers can also be found in the ^{19}F NMR spectra (Fig. 4). The peaks for each set of *o*-, *m*-, and *p*-F atoms further establish the fact the two perfluorophenyl rings of **5** have markedly different orientations from those of **3**.

Compound **7** was isolated from a similar oxidation reaction with tripyrrane **2** having 2,6-dichlorophenyl substituents on the *meso*-positions. The mass spectrum showed a parent peak in which two tripyrrines are bound to a dichloro-dicyano-diquinolate moiety. Single crystal X-ray data were collected from a sample of the material. The crystal was a particularly weak diffractor, with recognizable data out only

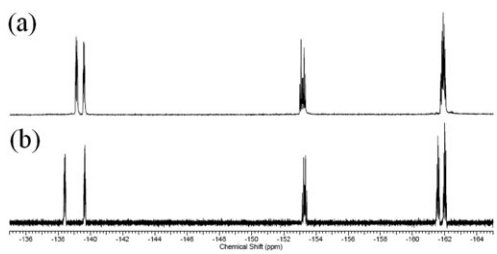

Fig. 4 ^{19}F NMR (282.4 MHz) spectra of **3** (a) and **5** (b).

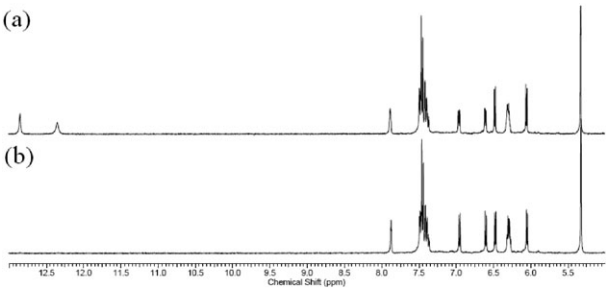

Fig. 5 ^{1}H NMR spectra of **7** in CD_2Cl_2; (a) before and (b) after adding D_2O.

as far as 37.5°, 2θ (Mo radiation). Although the data were weak an initial structure was obtained and isotropic refinements could be carried out. Subsequent anisotropic refinements were, predictably, unreliable, resulting in unreasonable geometries and anisotropic displacement parameters. The isotropic model is, however, sufficient to unambiguously determine the three-dimensional connectivity of the compound (see ESI†). A related structure, having similar connectivity to DDQ, has recently been obtained from the oxidation of a simple dipyrromethane.[5] The optical spectral data suggested that **7** contained an extended π-conjugated chromophore and the ^{1}H NMR requires a symmetrical configuration.

Since the diffraction data only confirmed the configuration we have carried out Kohn–Sham density functional theory (DFT) calculations on compound **7**. Both the observed and calculated ^{1}H NMR data show very similar chemical shifts (ESI†). The ^{1}H NMR spectrum of **7** (Fig. 5) supports the assigned structure where one set of α-H is absent (from the original tripyrrane) confirming connection to the DDQ adduct and showing that compound **7** has a symmetric structure in solution. Two sets of two doublets for the β-Hs on the inner pyrroles and one set of three broad peaks for the α- and β-Hs on the terminal pyrroles appear in the ^{1}H NMR and HHCOSY spectra (Fig. 5 and Fig. S19, ESI†). Similar to the observations for **3**, the amino-H peaks of **7** are hydrogen-bonded to the imino-N and the carbonyl-O resulting in pronounced downfield shifts (12.84 and 12.35 ppm). The energy minimized structure has C_2 symmetry and hydrogen-bonds as shown in Fig. 6. In CH_2Cl_2, **7** showed a major absorption band at 397 nm, which shifted to 423 nm upon protonation.† A broad absorption band around 700 nm indicates that the molecule is more extensively conjugated

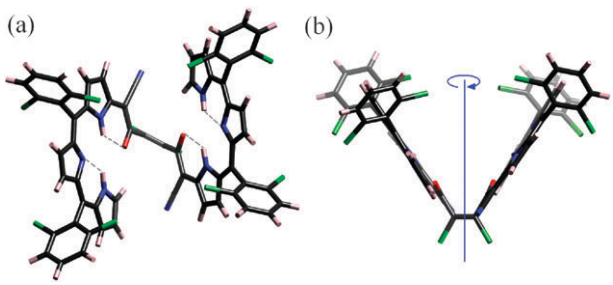

Fig. 6 Energy minimized structure of compound **7** (B3LYP/6-31G(d,p), Gaussian[6]); (a) top view and (b) side view. Hydrogen-bonds are indicated with dashed lines.

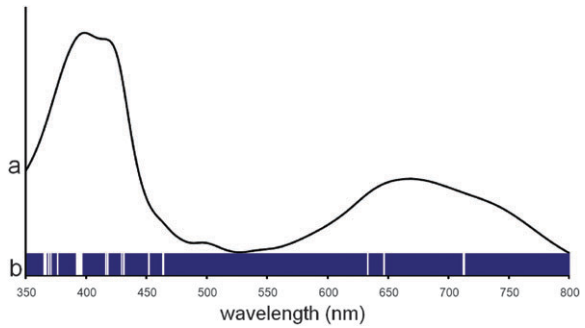

Fig. 7 Observed (a) and calculated (b) optical spectra of compound **7** in CH_2Cl_2.

than the tripyrrin; the calculated optical spectrum also supports this extended conjugation. Both the observed and calculated electronic spectra are congruent (Fig. 7).†

An understanding of the mechanism for the formation of these compounds remains an important issue and further research is continuing.

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Notes and references

‡ Selected data for **3**: 23% yield, λ_{max} (CH_2Cl_2)/nm 339.0, 541.1; ^{1}H NMR (600 MHz, CD_2Cl_2) δ = 11.58 (br s, 1H, NH), 10.01 (br s, 1H, NH), 7.51 (s, 1H, αH), 6.85 (d, J = 5.7, 1H, βH), 6.75 (d, J = 4.7, 1H, αH), 6.43 (s, 1H, βH), 6.42 (d, J = 3.8, 1H, βH), 6.35 (d, J = 5.7, 1H, βH), 6.28 (d, J = 4.8, 1H, βH); ^{19}F NMR (282.4 MHz, CD_2Cl_2) δ = −139.13 (dd, J = 8.6, ^{dd}J = 23.6, 2F, *o*-F), −139.61 (dd, J = 6.5, ^{dd}J = 19.3, 2F, *o*-F), −153.07 (t, J = 21.5, 1F, *p*-F), −153.25 (t, J = 21.5, 1F, *p*-F), −161.88 (m, 4F, *m*-F); ^{13}C NMR (150.96 MHz, CD_2Cl_2) δ = 171.77, 167.13, 151.14, 144.53, 147–137, 136.76, 135.23, 132.15, 131.95, 129.13, 127.73, 126.62, 124.41, 122.96, 113.98, 112.5–110.5 (the peaks are broadened by the multiple ^{13}C–^{19}F couplings of the perfluorophenyl rings), 101.71; *m*/*z* EIMS found 570.0674, calc. 570.0664 for $C_{26}H_{10}N_3OF_{10}$ ([M + H$^+$]$^+$). Selected data for **4**: 5% yield, ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 11.43 (br s, 1H, NH), 9.91 (br, 1H, NH), 7.45 (m, 5H, aryl-H and αH), 7.39 (dt, J = 7.0, ^{dt}J = 9.0, aryl-H), 6.71 (d, J = 5.5, 1H, βH), 6.57 (d, J = 4.3, 1H, βH), 6.37 (dd, J = 3.9, ^{dd}J = 1.6, βH), 6.28 (dd, J = 4.5, ^{dd}J = 1.0, βH), 6.26 (d, J = 5.9, βH), 6.08 (d, J = 4.7, βH); *m*/*z* ESIMS found 526.0045, calc. 526.0047 for $C_{26}H_{16}N_3OCl_4$ ([M + H]$^+$). Spectral data for **5**: 10% yield, ^{1}H NMR (300 MHz, CD_2Cl_2) δ = 12.03 (br s, 1H, NH), 8.06 (dd, J = 5.8, ^{dd}J = 1.4, 1H, αH), 8.00 (br s, 1H, NH), 7.35 (s, 1H, αH), 6.74 (d, J = 4.7, 1H, βH), 6.50 (d, J = 4.7, 1H, βH), 6.39 (dd, J = 6.0, ^{dd}J = 1.7, 1H, βH), 6.37 (m, 1H, βH), 6.36 (s, 1H, βH); ^{19}F NMR (282.4 MHz, CD_2Cl_2) δ = −138.40 (d, J = 17.2, 2F, *o*-F), −139.67 (dd, J = 4.1, ^{dd}J = 8.9, 2F, *o*-F), −153.24 (t, J = 20.6, 1F, *p*-F), −153.25 (t, J = 21.5, 1F, *p*-F), −161.51 (m, 2F, *m*-F), −161.98 (m, 2F, *m*-F); ^{13}C NMR (75.48 MHz, CD_2Cl_2) δ = 171.64, 164.64, 150.01, 144.02, 147–137 (the peaks are broadened by the multiple ^{13}C–^{19}F couplings of the perfluorophenyl rings), 137.27, 134.54, 132.88, 132.27, 127.96, 126.14, 122.68, 119.57, 113.96; *m*/*z* ESIMS (+ev) found 570.0, calc. 570.1 for $C_{26}H_{10}N_3OF_{10}$ ([M + H$^+$]$^+$), (−ev) found 567.9, calcd. 568.1 for $C_{26}H_8N_3OF_{10}$ ([M − H$^+$]$^-$). Selected data for **6**: <0.5% yield, *m*/*z* ESIMS found 526.0052, calc. 526.0047 for $C_{26}H_{16}N_3OCl_4$ ([M + H$^+$]$^+$). Selected data for **7**: 30% yield, ^{1}H NMR (300 MHz, CD_2Cl_2) δ = 12.84 (br s, 2H, NH), 12.35 (br s, 2H, NH), 7.88 (s, 2H, αH), 749–7.36 (m, 12H, aryl-H), 6.95 (dd, J = 5.5, ^{dd}J = 1.7, 2H, βH), 6.60 (d, J = 5.5, ^{dd}J = 1.7, 2H, βH), 6.47 (d, J = 4.4, 2H, βH), 6.33 (m, 2H, βH), 6.29 (m, 2H, βH), 6.05 (d, J = 4.4, 2H, βH); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 183.02, 163.12, 162.38, 151.55, 143.38, 138.86, 138.57, 136.80, 136.09, 135.94, 134.87, 134.73, 134.16, 134.07, 132.71, 131.53, 131.11, 128.86, 128.57, 127.72, 127.03, 126.09, 124.47, 117.68, 114.82, 83.03; *m*/*z* found 1248.1, calc. 1247.9 for $C_{60}H_{32}Cl_{10}N_8O_2$ (M$^+$).

§ Crystal data for **3**: $C_{26}H_9F_{10}N_3O{\cdot}1/2CH_2Cl_2$, m = 611.83, monoclinic, a = 29.240(1) Å, b = 23.151(9) Å, c = 7.016(2) Å, β = 93.06(1)°, V = 4743(3) Å^3, T = 173 K, space group C_2/c (no. 15), z = 8, λ(Mo-Kα) = 2.69 cm^{-1}, 16 039 reflections measured, 8018 unique which were used in all calculations. The data were corrected for Lorentz and polarization effects and absorption (multi-scan including decay and scaling relative correction factors 0.681–0.987). The structure was solved by direct methods (SIR92). The final refinement converged at R_1 [F, 7238 reflections having $I > 2.00\sigma(I)$] = 0.084 and wR_2(F^2, all 13 171 unique reflections) = 0.246. All refinements were performed using the SHELXTL crystallographic software package of Bruker-AXS. This particular structure was twinned, and the data set used to refine the structure had reflections from both components. This makes it look as though there are more reflections than are necessary.

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