Structural Diversity in Rubyrins: X-ray Structural Characterisation of Planar and Inverted Rubyrins

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Meso aryl rubyrins exhibit three different structures. A planar (**7**) and two unusual inverted structures (**8** and **9**) have been characterised by X-ray and NMR spectroscopy.

Introduction

Rubyrins **1** are a class of expanded porphyrins in which six pyrrole rings are linked in a cyclic 1.1.0.1.1.0 fashion. The other hexapyrrolic systems reported to date include hexaphyrin (1.1.1.1.1.1) **2**, bronzaphyrin (2.0.0.2.0.0) **3**, rosarin (1.0.1.0.1.0) **4** and amethyrin (1.0.0.1.0.0) **5** (Scheme 1). Of these only **1**, **2** and **3** were found to be aromatic with 26 π-electrons.[1] The X-ray structure of **1** in its diprotonated form reveals a planar structure with only a slight deviation of the pyrrole rings from the mean plane.[2] A common structural feature among these compounds is the presence of β-substituents on the pyrrole units with free meso carbons, with the exception of **4** where additional meso phenyl rings are also present. Very recently, the synthesis of meso aryl hexaphyrin **6** and its hydrogenated form has been achieved; the X-ray structure reveals that the two opposite pyrrole rings are inverted.[3]

We have recently reported the structures of core modified meso aryl sapphyrins and have shown that these molecules show structural diversity.[4] Two types of structures, normal and inverted sapphyrins, have been established. Latos-Grazynski and co-workers[5] were the first to predict the existence of such structures in sapphyrins based on spectroscopic data.

This observation led us to anticipate that the meso aryl rubyrins should also exhibit such structural diversity, and, indeed, meso aryl rubyrins exhibit three different structure types: planar **(7)**, inverted **(8)** in which the heterocyclic rings linking the two bipyrrole units are inverted and another form of inverted structure **(9)** in which one of the pyrrole rings of each bipyrrole unit is inverted (Scheme 2). The details of these results are reported in this communication.

Results and Discussion

The synthesis of **7** and **8** has recently been reported.[6] Compound **9** was synthesised by a self-condensation reaction of 5,10-dimesityl-16-oxatripyrrane by a similar method in 12% yield.

The single crystal X-ray structure of **7** (Figure 1a) reveal that the molecule is almost planar with only small deviation from the mean plane.[7] Specifically, one of the selenophene rings of the bis-selenophene unit is deviated by 6.18°, whilst the other deviates by 1.45° from the mean rubyrin plane. The pyrrole rings show a deviation of 4.85°. On the other hand, compound **8** shows an inverted structure[8] (Figure 1b) where the furan and thiophene rings which connect two bipyrrole units on either side undergo a 180° flipping resulting in the appearance of the β-CH protons in the ring current while the heteroatoms O and S are drawn away from the ring current of the macrocycle. Due to the high symmetry of the molecule there is disorder in the crystal. The thiophene and the furan rings are tilted above and below the rubyrin mean plane making the molecule nonplanar. Specifically, the torsional angles between the planes defined by the meso carbon atoms C5, C10, C5′ and C10′ and the planes defined by the rings containing O1/S1, N1 and N2 are 32.59°, 10.48° and 3.15°, respectively. Furthermore, two molecules of methanol are trapped above the rubyrin plane with two hydrogen bonding interactions. [N1−H17···O2 2.848(3) Å, 150(2)° and O3−H25···N2 2.733(2) Å, 153(2)°]. The ring inversion in **8** leads to a reduction in the inner core relative to **7** and the diprotonated salt of **1**. This was inferred from the angles C4−C5−C6 [119.9(2)°] and C9−C10−C11 [119.5(2)°] (these angles for **7** and the dihydrochloride salt of **1** are 124.4(10)°, 125.2(10)°, and 137.0°, 137.63° respectively). Furthermore, the ring inversion results in an increase in the distance between the two bipyrrole units (N1−N2 6.492 Å) and a decrease in the distance

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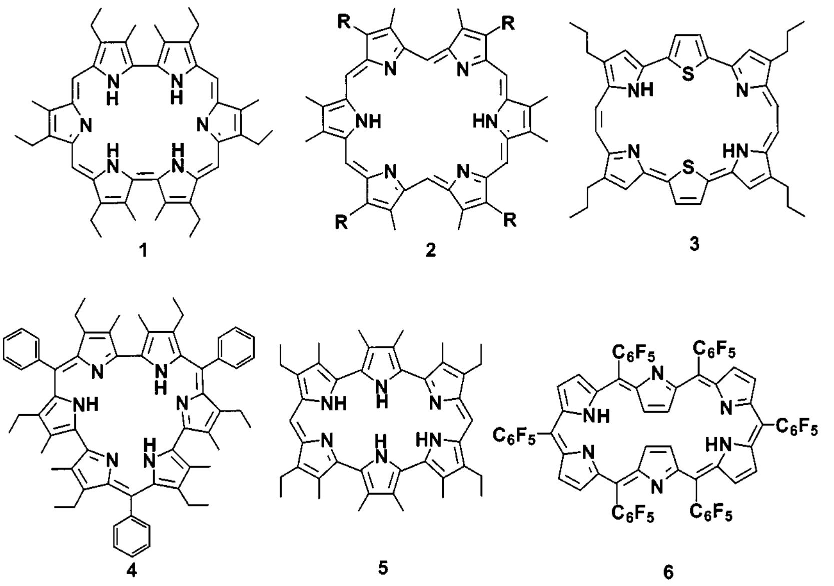
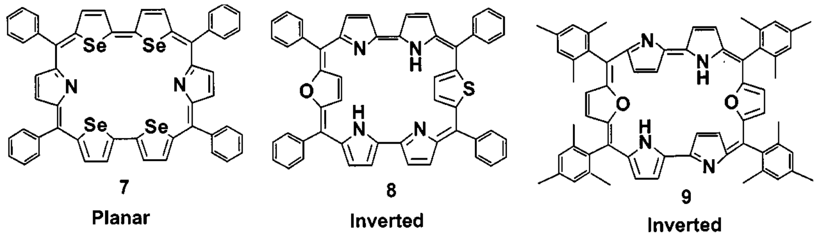


Scheme 1. Macrocycles containing six heterocyclic rings



Scheme 2. Core-modified rubyrins with planar and inverted structures

between the two adjacent nitrogens in the bipyrrole unit (N1−N2′ = 2.787 Å) relative to **7** and the dihydrochloride salt of **1** (the corresponding distances are Se1′−Se2 = 3.468 Å, Se1−Se2 = 3.566 Å for **7** and N1−N3 = 5.559 Å, N1−N3′ = 3.078 Å for **1**]. In both cases the $C_\alpha-C_\beta$ distances are larger than $C_\beta-C_\beta$ distances suggesting the aromatic nature of the macrocycle.

Since it was not possible to get good quality crystals, the structure of **9** was deduced from its ^{1}H NMR spectrum (Figure 2). The assignments are marked in the spectrum and were made using the correlations in the ^{1}H-^{1}H COSY spectra. All the signals were broadened due to the poor solubility of **9**. However, sharp, well-resolved signals were obtained upon protonation with TFA. There are two sets of doublets of doublets of equal intensity in the region δ = 8.5 to 10 assigned to four furan protons (e and f) and four pyrrole protons (a and b). The β-CH protons of the inverted pyrrole ring resonate as a doublet of doublets (Figure 2 inset) between $\delta = -1.8$ to -2.0 and the inner −NH proton of the pyrrole ring appears at $\delta = -2.63$. Generally, in rubyrins the inner pyrrole −NH protons are not observed at room temperature because of the rapid tautomerism[6c] between the two adjacent nitrogens in the bipyrrole unit. The fact that a sharp resonance is seen for the inner −NH protons in **9** at room temperature suggests localisation of these protons thus ruling out any tautomerism. This is possible because of the inversion of the other pyrrole unit where the pyrrole nitrogen is pointing away from the inner core. This is further substantiated by protonation of the inverted pyrrole nitrogen where a signal at δ = 16 is observed for the −NH proton. On the other hand the NMR studies reveal that the protonation of **8** leads to a 180° ring flipping of both thiophene and furan rings bringing the molecule back to a planar structure. To the best of our knowledge this unusual inverted structure of **9** is unprecedented in the literature. Preliminary metallation studies reveal coordination of the inverted pyrrole nitrogen to the metal in **9**. Studies in this direction are in progress.

In conclusion, it has been clearly shown that the meso aryl rubyrins show an interesting structural diversity which is unknown for the β-substituted rubyrins.

Experimental Section

Selected Data for 9: UV/Vis: λ_{max} (CH_2Cl_2/5% triethylamine) (log ε) = 519 (5.15), sh543 (5.04), 689 (4.15), 749 (4.36), 862 (3.71), 989 (4.55) nm; λ_{max}(CH_2Cl_2/5% TFA)/nm (log ε) = 516 (5.37), 568 (5.03), 707 (4.27), 780 (4.06), 830 (4.02), 937 (4.91) nm. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = −2.63 (s, 2 H), −2.00 (d, 2 H), −1.90 (d, 2 H), 1.85 (s, 12 H), 2.00 (s, 12 H), 2.64 (s, 6 H), 2.67 (s, 6 H), 7.34 (s, 4 H), 7.40 (s, 4 H), 8.66 (d, 2 H), 8.91 (d, 2 H), 9.04 (d, 2 H), 9.86 (d, 2 H); ^{1}H NMR (300 MHz, CD_2Cl_2/TFA): δ = −3.49 (s, 2 H), −2.95 (d, ^1J = 5.6 Hz, 2 H), −2.60 (d, ^1J = 5.2 Hz, 2 H), 1.98 (s, 12 H), 2.05 (s, 6 H), 2.67 (s, 6 H), 3.61 (s, 12 H), 7.44 (s, 4 H), 7.46 (s, 4 H), 9.04 (dd, ^1J = 5.0 Hz, ^3J = 2.0 Hz, 2 H), 9.53 (d, ^1J = 5.2 Hz, 2 H), 9.54 (d, ^1J = 5.2 Hz, 2 H), 9.04 (dd, ^1J = 5.2 Hz,

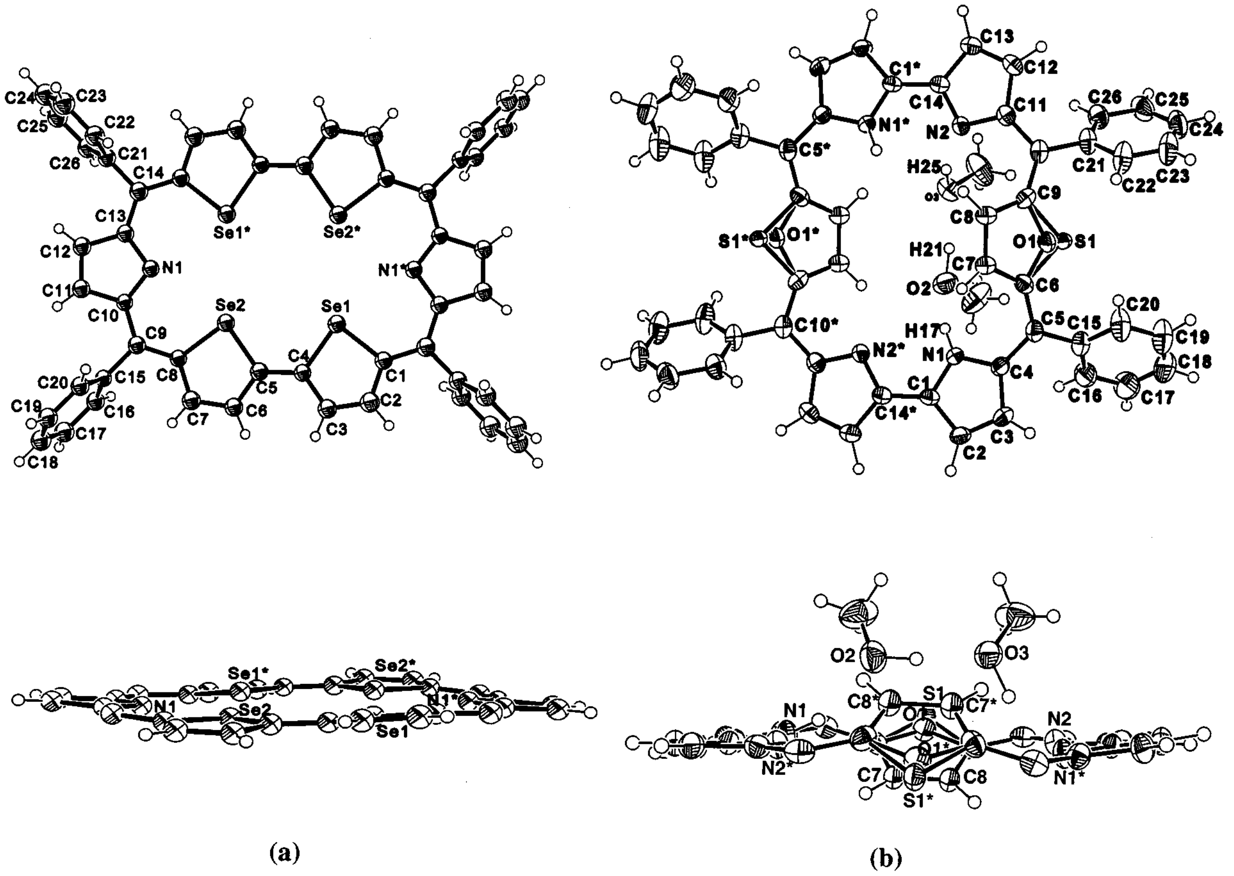


Figure 1. Two views of the molecular structure of **7** (a) and **8** (b); the phenyl rings are omitted for clarity in the side view

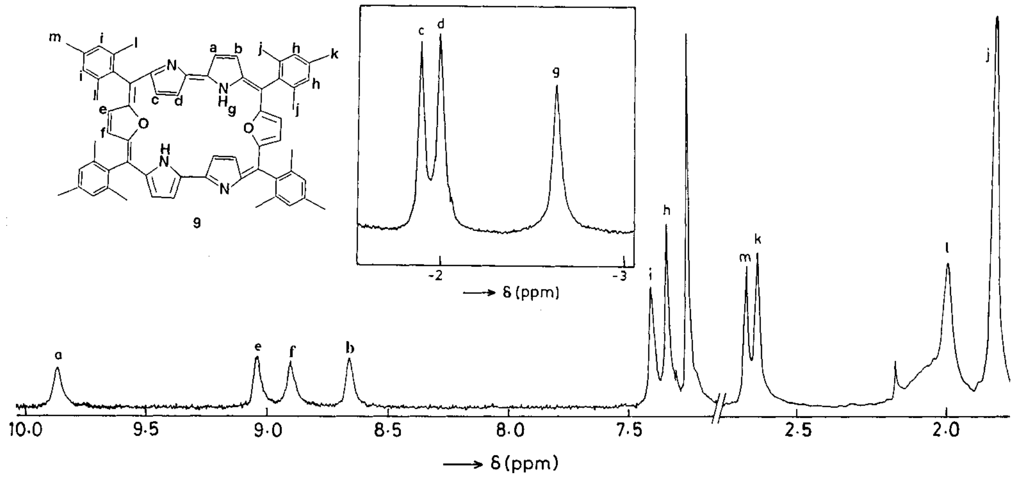


Figure 2. ^1H NMR ($CDCl_3$) spectra of **9**; the inset shows the inner β-CH and -NH proton resonances in the ring

^3J = 2.0 Hz, 2 H); ^1H NMR (300 MHz, CD_2Cl_2/TFA): δ = −3.75 (s, 2 H), −3.00 (d, ^1J = 2.2 Hz, 2 H), −2.77 (d, ^1J = 2.2 Hz, 2 H), 1.27 (s, 6 H), 7.48 (s, 24 H), 2.70 (s, 6 H), 7.48 (s, 4 H), 7.53 (s, 4 H), 9.21 (dd, ^1J = 2.8 Hz, ^3J = 1.1 Hz, 2 H), 9.68 (d, ^1J = 2.8 Hz, 2 H), 9.73 (d, ^1J = 2.8 Hz, 2 H), 9.82 (dd, ^1J = 2.8 Hz, ^3J = 1.1 Hz, 2 H), 13.91 (s, 2 H). − ESMS: m/z = 915 [M^+]. − $C_{64}H_{58}N_4O_2$: C 83.99, H 6.39, N 6.12; found C 83.86, H 6.35, N 6.06.

Acknowledgments

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[7] Crystal data for $C_{105}H_{66}Cl_2N_4Se_8$ (**7**): M = 2086.29, monoclinic, a = 13.193(4), b = 12.492(7), c = 26.804(8) Å, β = 102.98(3)°, V = 4304(2) Å^3, T = 226 K, space group $P2_1/a$ (no. 14), Z = 2, μ (Mo-K_{α}) = 35.11 cm^{-1}, 14970 reflections measured, 8172 unique (R_{int} = 0.075), the final R = 0.069 and R_w = 0.077. A gold plate of Se_4N_2 rubyrin was obtained by diffusing methanol into a dichloromethane solution of **6**. All the measurements for the crystal structures reported in this paper were made on a Rigaku AFC&R diffractometer with graphite monochromated Mo-K_{α} radiation and a rotating anode generator. The structures were solved using direct methods and refined by full-matrix least-squares.

[8] Crystal data for $C_{63}H_{55}N_5O_5S$ (**8**): M = 994.22, monoclinic, a = 34.484(5), b = 10.593(3), c = 15.899(4) Å, β = 114.37(1)°, V = 5290(2) Å^3, T = 226 K, space group $C2/c$ (no. 15), Z = 4, μ (Mo-K_{α}) = 1.17 cm^{-1}, 6180 reflections measured, 6083 unique (R_{int} = 0.019), the final R = 0.063 and R_w = 0.074. Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136539 (**7**) and -136538 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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