Serendipitous Desymmetrisation during Porphyrazine Synthesis: an X-Ray Crystallographic Study of 2,3,7,8,12,13,17,18-Octakis(dimethylamino)-2-secoporphyrazine-2,3-dione

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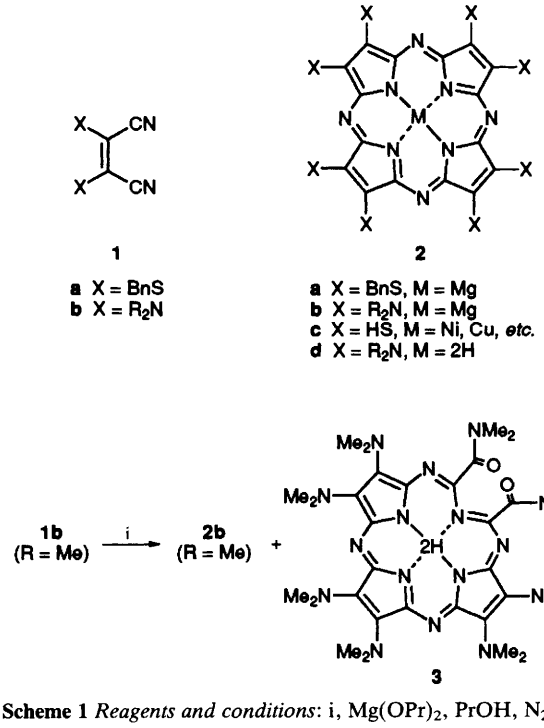
Linstead macrocyclisation of 2,3-bis(dimethylamino)2(*Z*)-butenedinitrile gives [2,3,7,8,12,13,17,18-octakis(dimethylamino)porphyrazato]magnesium(II) and the title seco-porphyrazine, the structure of which is established by an X-ray crystallographic study.

Recently, we have reported the synthesis and characterisation of the porphyrazine octathiolate and porphyrazinoctamine derivatives **2a** and **b** (R = Me, Bn, *etc.*) by macrocyclisation of the maleonitrile derivatives **1** using magnesium propoxide in propanol.[1–3] Transmetallation and debenzylation of complex **2a** gave the corresponding octathiols **2c** and these substances were converted into star porphyrazines by peripheral metallation *via* quadruple tridentate (S-*meso*-N–S)[1] or bidentate (S–S)[2] coordination. During several Linstead macrocyclisation reactions[4] to provide **2a** and **b**, we noted the formation of other minor porphyrazine-like compounds with tantalising intense colours. Herein we report the full characterisation of the major by-product in the conversion of 2,3-bis(dimethylamino)-2(*Z*)-butenedinitrile (**1b**, R = Me)[5] into the porphyrazine **2b** (R = Me). Much to our surprise the side reaction involves desymmetrisation and loss of the magnesium(II) cation.

Treatment of 2,3-bis(dimethylamino)-2(*Z*)-butenedinitrile (**1b**, R = Me) with magnesium propoxide in propanol at reflux[4] gave the purple porphyrazine **2b** (R = Me, 48%) and traces of a less polar purple pigment (Scheme 1). In a control experiment, demetallation of the porphyrazine **2b** (R = Me) using glacial acetic acid in the presence of air gave the same pigment (62%). In contrast, anaerobic demetallation of the magnesium complex **2b** (R = Me) gave only the porphyrazine **2d** (R = Me, 69%). The spectroscopic signature of this substance† was most curious. Firstly, both the ^1H and ^{13}C



Scheme 1 *Reagents and conditions*: i, $Mg(OPr)_2$, PrOH, N_2, heat

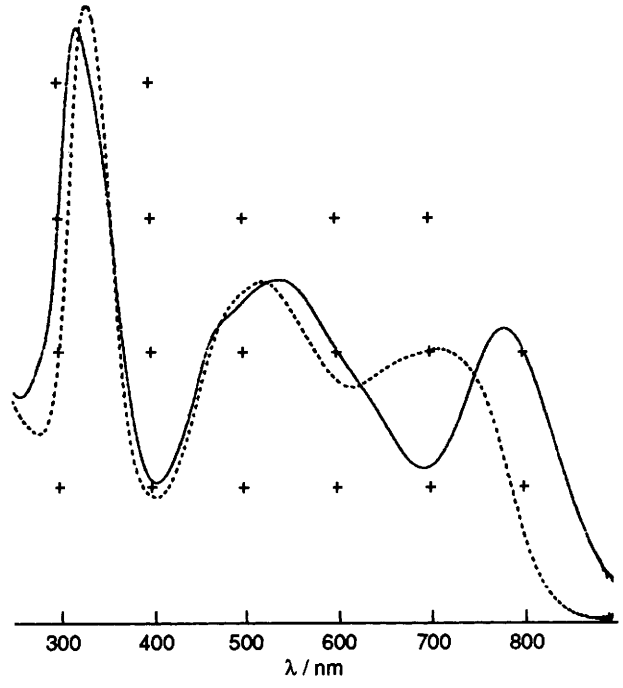


Fig. 1 UV–VIS spectra of seco-porphyrazine **3** (–) and porphyrazine **2d** (---) (R = Me)

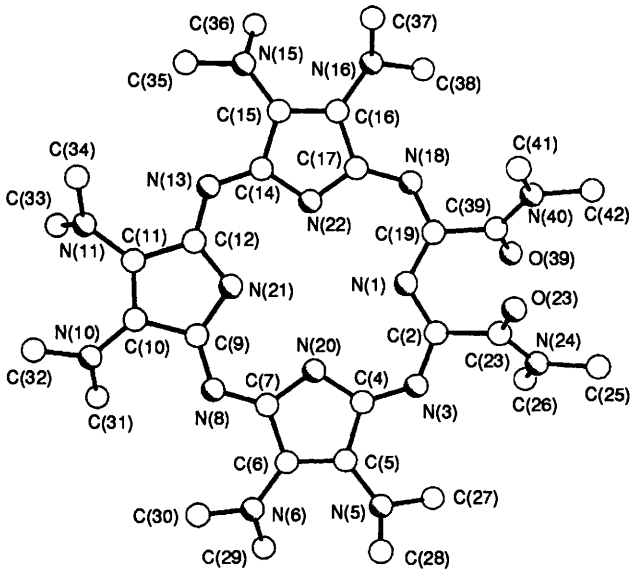


Fig. 2 X-Ray crystal structure of 2,3,7,8,12,13,17,18-octakis(dimethylamino)-2-secopoporphyrazine-2,3-dione

NMR spectra showed that the compound lacked the expected D_{4h} symmetry of the (porphyrazinato)magnesium(II) complex. Both microanalysis and high resolution mass ion measurement were consistent with a composition of $C_{32}H_{50}N_{16}O_2$. The UV–VIS spectrum (Fig. 1) also showed a loss of symmetry with the shift of the Q band from 709 to 788 nm. It is clear from these results that the purple macrocycle had readily desymmetrised and lost the magnesium(II) cation.

Recrystallisation of the purple pigment from ethyl acetate and hexanes gave black crystals with green reflections suitable for an X-ray crystallographic study.‡ (Fig. 2) This study unequivocally established the structure of the purple pigment as the seco-porphyrazine **3**. The ^{1}H and ^{13}C NMR spectra for this substance show five distinct *N*-methyl groups, six ring carbons and an amide carbonyl. These features are fully consistent with structure **3** and with slow rotation about the amide units. It is reasonable to speculate that the seco-porphyrazine **3** arose *via* singlet oxygen mediated ring scission of a single pyrrole entity.

Clearly pigment **3** represents a novel macrocyclic ring system. Further aspects of porphyrazine-octathiol and -octaamine chemistry will be reported in due course.

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Footnotes

† *Data* for **3**: mp 280–285 °C (EtOAc–hexanes); TLC 0.31 (EtOAc:hexanes 3:2); IR ν_{max} (CH_2Cl_2)/cm^{-1} 3053, 2927, 1639, 1577, 1519, 1265, 729, 709; UV–VIS (CH_2Cl_2) λ max/nm (log ε) 322 (4.76), 485 (4.47), 542 (4.53), 783 (4.46); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 12H), 3.76 (s, 6H), 3.54 (s, 12H), 3.42 (s, 12H), 3.30 (s, 6H), 0.05 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 154.7, 153.4, 141.0, 139.3, 136.4, 129.7, 45.3, 45.2, 43.9, 40.2, 35.3; HRMS (FAB) *m/z* calc. for $C_{32}H_{50}N_{16}O_2$: (M^+), 690.4303. Found: 690.4318. Found: C, 55.84; H, 7.05; N, 32.17. Calc. for $C_{32}H_{50}N_{16}O_2$: C, 55.62; H, 7.30; N, 32.45%.

‡ *Crystal data* for **3**: $C_{32}H_{50}N_{16}O_2$, M = 690.9, triclinic, a = 6.270(4), b = 11.210(7), c = 14.108(9) Å, α = 103.90(2), β = 102.77(2), γ = 101.46(2)°, V = 905 Å^3, space group $P1$, Z = 1, D_c = 1.27 g cm^{-3}, μ(Cu-Kα) = 7.0 cm^{-1}, $F(000)$ = 370. A dark green iridescent platy needle of dimensions 0.12 × 0.37 × 0.97 mm was used. Data were measured on a Siemens P4/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically to give R = 0.046, R_w = 0.053 for 2785 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 130°$]. The structure is partially disordered with *ca.* 20% of the molecules inverted about the centre of the porphyrazine ring. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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