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Cyclisation Involving a *meso*-Phenyl Substituent of a Metalloporphyrin: X-Ray Structure of 5,10,15-Triphenyl{2^2-oxo-benzo$[2^32^4]$cyclohexa[a,b]porphinato(2–)}copper(II)

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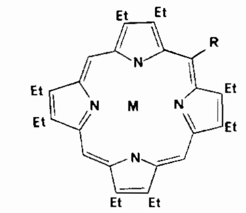
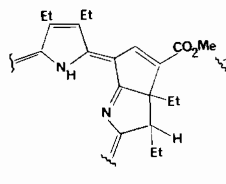
Reactions have been reported [1, 2] in which porphins with unsaturated groups in the *meso*-position form an isocyclic ring fused to the β-pyrrole carbon, and it has been suggested [1, 2] that steric overcrowding is a necessary condition for the cyclisation. For example, in the octaethylporphyn series, the unsaturated dicarboxylic acid monomethyl ester (Ia) gave the purpurin (II) on heating in toluene, while treatment of the diacid (Ib) with H_2SO_4 gave the verdin (III) [1]. Similar H_2SO_4 reaction of thc *meso*-acrylaldehyde (Ic) was shown by an X-ray study to give the cyclised product (IV) [2].



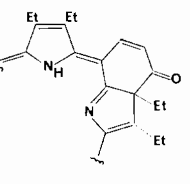
(Ia) $R = -CH{=}C\genfrac{}{}{0pt}{}{CO_2Me}{CO_2H}$; M = 2 H

(Ib) $R = -CH{=}C(CO_2H)_2$; M = 2 H

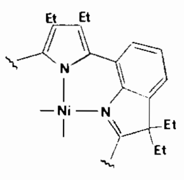
(Ic) $R = -CH{=}CH{-}CHO$; M = Ni(II)



II



III

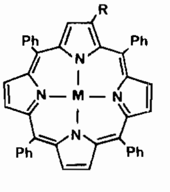


IV

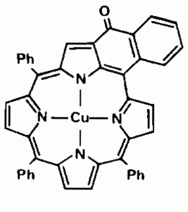
We report here a different type of cyclisation which has been observed in the tetraphenylporphyrin (TPP) series in which the ortho-position of one of the phenyl groups reacts with a β-formyl group, leading to a triphenylporphyrin with a fused benzocyclohexenone ring. *meso*-Triphenylporphyrins [3] have been recently synthesised *via* homoporphyrins [4].

Vilsmaier formylation (DMF/$POCl_3$ in $CHCl_3$, 65 °C, 16 h) of Cu(TPP) (Va) gave the formylporphyrin complex (Vb) in 94% yield [λ_{max}/toluene: soret 432 (ε, 302.7 ml mol^{-1} cm^{-1}), 521 (4.34), 553 (15.93), 594 (9.73) nm] which has a C=O stretching frequency (1661 cm^{-1}) in a similar position to that reported [5] for the corresponding nickel(II) complex (Vc). An attempt to demetallate (Vb) by treating with trifluoroacetic acid (60 °C, 1 h), followed by hydrolysis gave a mixture from which a small quantity of a deep green compound, the verdin (VI) was isolated. The compound (VI) was shown by field desorption mass spectrometry to have the molecular formula $C_{45}H_{26}CuN_4O$ (m/e 701), *i.e.* with two fewer hydrogenatoms than the precursor (Vb), $C_{45}H_{28}CuN_4O$ (m/e 703). The visible spectrum of (VI) [λ_{max}/toluene: soret 465 (ε 70.9 ml mol^{-1} cm^{-1}), 486 sh (27.8), 590 (2.9), 651 (7.25), 694 (5.85) nm], differs considerably from that of (Vb) but the continued presence of a carbonyl group is indicated by an IR band at 1651 cm^{-1}.

During the course of this work, other workers [6] have independently reported the synthesis of (Vb) and found that demetallation of (Vb) under various H_2SO_4 conditions did not lead to the corresponding free base (Vd) but gave a mixture which was not characterised.



Va M = Cu, R = H
Vb M = Cu, R = CHO
Vc M = Ni, R = CHO



The presence of the new fused benzocyclohexenone ring in (VI) was demonstrated by X-ray structure determination (Fig. 1). This shows that the benzene ring involved is now constrained to lie close to the plane of the porphin skeleton (Fig. 2). The unsaturated fused six-membered ring has been proposed [7] for the verdins [8] which have a characteristic strong absorption band at 695–698 nm. Bond lengths and angles within the copper verdin skeleton are comparable with those [9] of (Va) and

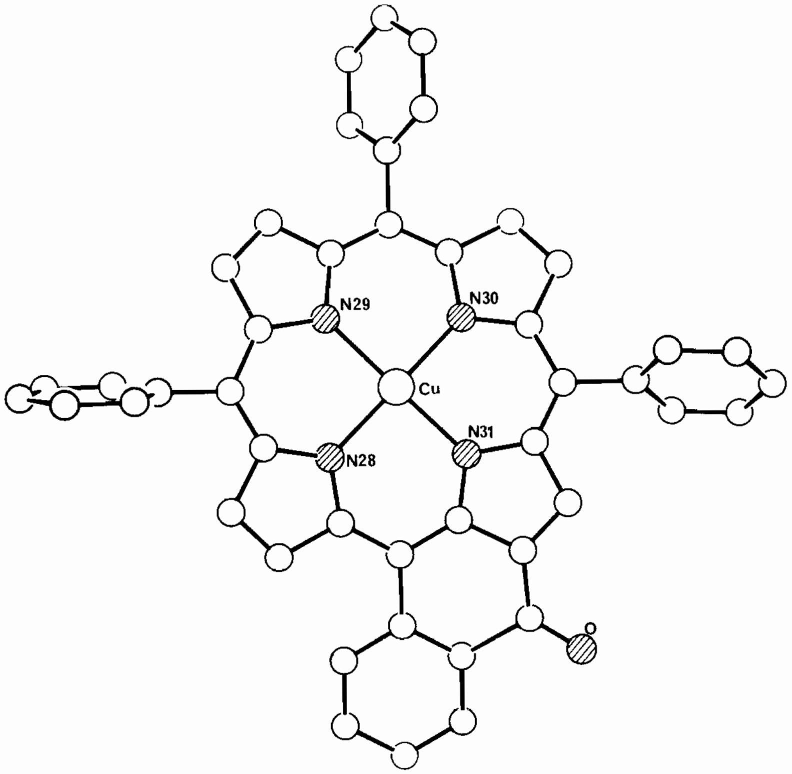


Fig. 1. The molecular structure of the verdin (VI). Bond lengths to the Cu atom (Å) are: N(28), 1.986(13); N(29), 1.972(13); N(30), 2.007(11); N(31), 2.010(12), and angles subtended at the copper atom by pairs of nitrogen donors are: N(28), N(29) 90.9(6); N(28), N(30) 178.8(6); N(28), N(31) 88.5(6); N(29), N(30) 89.5(6); N(29), N(31) 179.0(6); N(30), N(31) 91.(6)°.

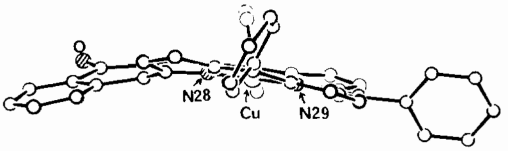


Fig. 2. The conformation of the fused benzocyclohexenone ring with respect to the porphin skeleton of (VI).

call for no special comment. The precision of the structure determination of (VI) does not allow a realistic assessment to be made of the importance of limiting Kekule formulae which have been proposed [7] to account for the long-wave spectra for the green chromophore in related compounds.

Experimental

Reaction of 2-Formyl-5,10,15,20-tetraphenylporphinatocopper(II), (Vb) with CF_3COOH

A suspension of (Vb) (13.25 g) in CF_3COOH (250 cm^3) was heated at 65 °C for 1 h. The resulting green solution was filtered into water (1500 cm^3) and the dark green precipitate which formed was collected by filtration, washed with water (6 × 250 cm^3), saturated EDTA solution (6 × 250 cm^3) and the residue dissolved in $CHCl_3$ (500 cm^3) containing Et_3N (10 cm^3). The green-brown $CHCl_3$ solution was washed with water (2 × 750 cm^3) and dried ($MgSO_4$). The $CHCl_3$ solution was then passed through a bed of alumina (Koch Light, type H). Evaporation of the eluate gave a semi-solid which was collected by slurrying with $CHCl_3$:EtOH (1:9, 150 cm^3) and filtered to give a solid (11.4 g). The filtrate was stored at room temperature and fine black-green needles were collected by refiltration, 15 mg of (VI). The bulk of the product was shown by TLC and IR to be a mixture consisting mainly of unchanged (Vb).

Crystal data for $C_{45}H_{26}CuN_4O$ (VI)

Monoclinic, space group $P2_1/n$, $a = 18.532(5)$, $b = 7.335(5)$, $c = 23.932(5)$ Å, $\beta = 93.26(2)°$ and $Z = 4$. The intensity data were collected with a Philips PW1100 four circle diffractometer, using graphite-monochromated Mo-K_α radiation. The structure was solved and refined [10] using 1339 unique reflections (θ range, 3–20°) with $I > 3\sigma(I)$; $R = 0.081$, after full matrix least squares refinement with 218 parameters. Anisotropic temperature factors were refined for the Cu and four N atoms only. The phenyl groups were constrained to have C–C = 1.395 Å and C–C–C = 120°, and the H atoms were set at C–H = 1.08 Å and $U = 0.10$ Å^2.

Acknowledgements

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8 The term isomesoverdin has been used [7] for compounds having the form of fusion of the cyclohexenone ring in (VI).

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