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Diels–Alder reactions of nickel(II) N-confused porphyrins as dienophiles†

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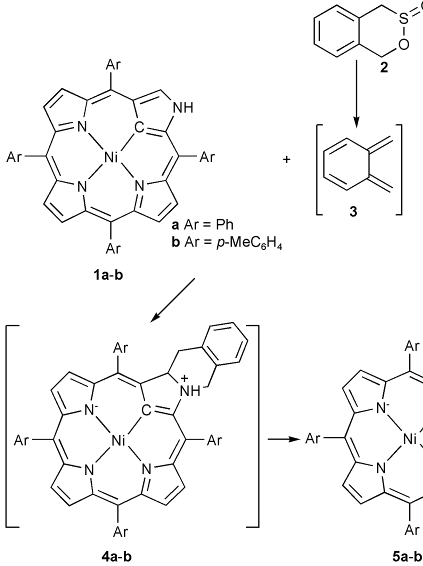
Received (in Corvallis, OR, USA) 16th April 2002, Accepted 18th June 2002
First published as an Advance Article on the web 19th July 2002

Diels–Alder reactions of nickel(II) N-confused tetraarylporphyrins as dienophiles with *o*-benzoquinodimethane yield nickel(II) N-confused isoquinoporphyrins.

An N-confused porphyrin is a porphyrin isomer with an inverted pyrrolic ring. Since the independent report of its preparation by Latos-Grazynski *et al.*[1] and Furuta *et al.*[2] in 1994, N-confused porphyrins have been studied for their ability to form complexes containing metal–carbon bonds as well as properties associated with the outward pointing nitrogen atom.

It is known that the peripheral double bonds of porphyrins are cross-conjugated and may react as alkenes,[3] and vinyl substituted porphyrins may react as dienes in Diels–Alder reactions.[4] Diels–Alder reactions of porphyrins as dienophiles have been reported by Cavaleiro *et al.*[5] Here we report on the reactions of the nickel(II) N-confused porphyrins (**1**) with *o*-benzoquinodimethane **3** to yield the nickel(II) N-confused isoquinoporphyrins **5** (Scheme 1).

N-Confused porphyrins were prepared using the procedure described by Lindsey *et al.*[6] and nickel(II) N-confused porphyrins were synthesized using the method of Latos-Grazynski *et al.*[1] A solution of nickel(II) N-confused tetraphenylporphyrin (**1a**, 100 mg) and sultine **2**[7] (1.50 g) was refluxed in benzene (50 mL) for 2 days. The solvent was removed by vacuum and the residue was chromatographed using silica gel (14 g, 1:1 hexanes/CH_2Cl_2). The product, which has a higher R_f value than that of **1a**,‡ was obtained in 23% yield and identified as the N-confused isoquinoporphyrin **5a** on the basis of its mass and NMR (^1H, ^{13}C, selective NOE, COSY and $^1H/^{15}N$ HSQC) spectra.§



Scheme 1

Based on correlations shown in a COSY experiment, the H^a/H^f protons appeared as singlets at δ 6.91 and 8.57 (see Scheme 1 for proton assignments) and the H^b–H^e protons appeared at δ 7.11, 7.27 (2H) and 7.46. The cross peak of ^1H δ 6.91 with ^{15}N δ 17 in the $^1H/^{15}N$ HSQC experiment showed that H^a is either two or three bonds away from a nitrogen atom, which indicates that cycloaddition occurred on the peripheral carbon–nitrogen bond rather than carbon–carbon bonds. The structure of compound **5b** is analogous to that of **5a**, as determined by NMR. Compounds **5a** and **5b** were presumably formed by oxidation of the chlorins **4a** and **4b**.

The high selectivity of the peripheral carbon–nitrogen bond over the carbon–carbon bonds can be rationalized by the resonance contributions to the overall structure of **1**.[8] Fig. 1 shows two such resonance structures. In canonical form **II** the C=N is both 'cross conjugated' and in an iminium form which is known to be electron-deficient and an active dienophile.[9] The original X-ray structure of **1b** was disordered[1] and the N(2) and C(21) atoms could not be distinguished. We have obtained the X-ray crystal structure of the N-iodooctyl derivative (**6**) and bond lengths (Fig. 2) clearly demonstrate the uniqueness of the $C=N^+R$ bond and confirm that it should be an effective dienophile.[9]

Direct evidence for the structural assignment of compound **5a** came from X-ray diffraction analysis (Fig. 3).¶ The isoquino group is in the same plane with the linked pyrrole subunit.‖ Unlike planar compound **1b**, the porphyrin skeleton of compound **5a** is ruffled. The dihedral angles between the pyrrole planes and the plane defined by N(22)N(23)N(24) are as follows: C(21) 19.88, N(22) 16.85, N(23) −15.98, N(24) −13.87°. The Ni–N(C) bond distances (Å) are: C(21) 1.904(2), N(22) 1.9239(18), N(23) 1.949(2), and N(24) 1.9276(18), which are shorter than that of compound **1b** (1.955 or 1.963 Å**), and this is a typical change from planar nickel(II) porphyrins to ruffled nickel(II) porphyrins.[10] The bond distance between N(2) and C(3) is 1.389(3) Å, much longer than that of

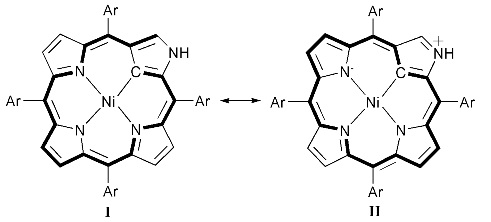


Fig. 1 Two canonical forms for a nickel(II) N-confused porphyrin.

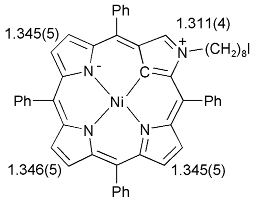


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Fig. 2 Peripheral bond lengths (Å) for compound **6**.

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† Electronic supplementary information (ESI) available: further characterization data. See http://www.rsc.org/suppdata/cc/b2/b203813g/

DOI: 10.1039/b203813g

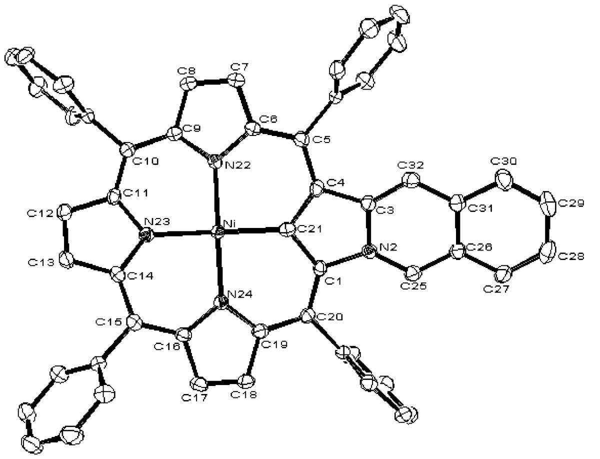

Fig. 3 An ORTEP drawing of compound **5a** showing atomic labeling and thermal ellipsoids at the 50% probability level.

compound **1b** (1.351 or 1.324 Å**), as N(2)–C(3) is in the isoquino group and has only about 1/3 double bond character.

In conclusion, the peripheral carbon–nitrogen double bonds of nickel(II) N-confused porphyrins are partially isolated from the 18π conjugated aromatic system and react as dienophiles in Diels–Alder reactions with *o*-benzoquinodimethane yielding novel nickel(II) N-confused isoquinoporphyrins. To the best of our knowledge, this is the first report on addition reactions of N-confused porphyrins.

We thank NSERC of Canada for funding, Dr Elizabeth Cheu for advice, and the departmental MS, NMR and Microanalysis for services.

Notes and references

‡ There is a compound with a higher R_f value than compound **5a**. The parent ion is observed at *m*/*z* 879 (LSIMS) suggesting the addition of two *o*-benzoquinodimethane. However, the amount was too small to be characterized by NMR spectroscopy.

§ R_f (silica–CH_2Cl_2/hexanes 2 : 1) 0.77; ^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 6.91 (s, 1H), 7.11 (d, J = 8.6 Hz, 1H), 7.27 (m, 2H), 7.46 (m, 1H), 7.55–8.05 (m, 20H), 8.22 (m, 2H), 8.29 (m, 3H), 8.36 (d, J = 4.9 Hz, 1H), 8.57 (s, 1H); UV-vis (CH_2Cl_2) λ_{max}/nm (log ε) 438 (5.07), 628 (4.62); MS (LSIMS) 770 (M, 100%); HRMS (LSIMS) *m*/*z* Calc. for $C_{52}H_{32}N_4Ni$: 770.19799. Found 770.19797 (M); Anal. Calc. for $C_{52}H_{32}N_4Ni{\cdot}0.5H_2O$: C, 80.02; H, 4.26; N, 7.18. Found: C, 79.88; H, 4.11; N, 6.95.

¶ Crystal data: $C_{52}H_{32}N_4Ni$ (**5a**), M = 771.53, monoclinic, a = 13.2484(19), b = 15.1197(17), c = 19.255(3) Å, β = 110.821(3)°, V = 3605.1(8) Å^3, T = 173(2) K, space group $P2_1/c$ (No. 14), Z = 4, μ(Mo-Kα) = 5.84 cm^{-1}, 33795 reflections measured, 8021 unique (R_{int} = 0.085) which were used in all calculations. The final $wR(F^2)$ was 0.0873 (all data). There is a 50/50 disorder between N(2) and C(3) for complex **5a** since N(2) and C(3) are occupied half the time by nitrogen and half the time by carbon. CCDC 169757. See http://www.rsc.org/suppdata/cc/b2/b203813g/ for crystallographic data in CIF or other electronic format.

‖ Deviation from plane for the isoquinopyrrole unit is 0.066 Å.

** The C(21) and N(2) atoms in complex **1b** are disordered and not distinguishable in the X-ray structure.[1]

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