Tetrahedron Vol. 49, No. 42, pp. 9489-9494, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00
Pergamon Press Ltd

Synthesis and Spectroscopic Investigation of Directly Azobenzene Bridged Diporphyrins

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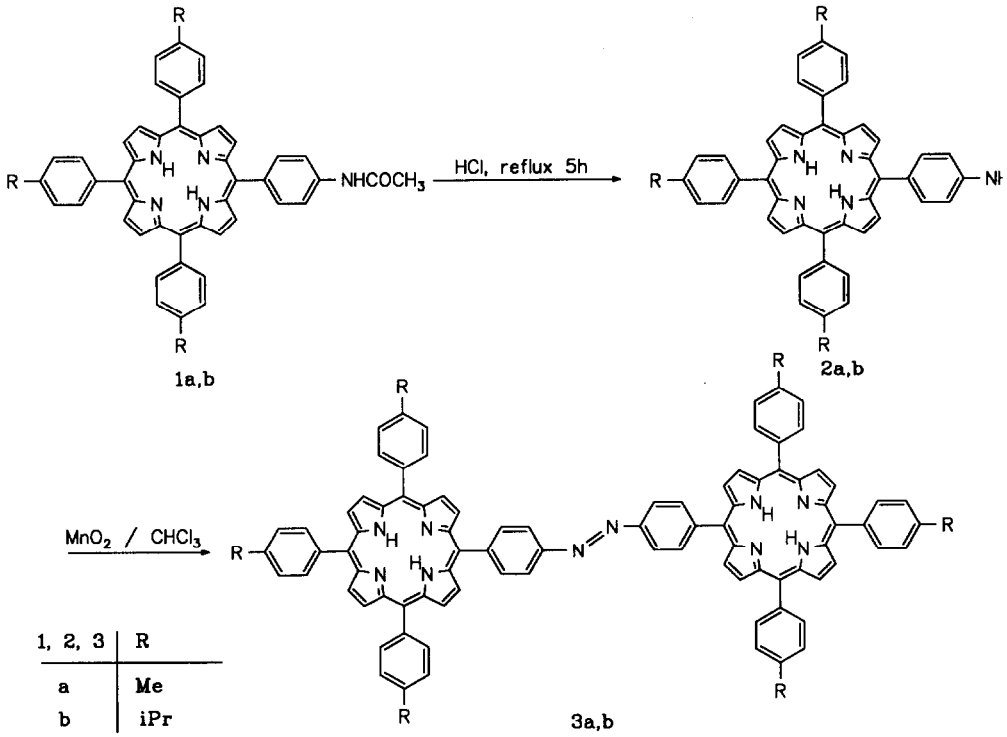
(*Received in Germany* 2 *July* 1993; *accepted* 5 *August* 1993)

Abstract: The synthesis of new directly azobenzene bridged diporphyrins is described. The spectroscopic properties of the new compounds are discussed.

Since the last two decades, there is a growing interest in porphyrin synthesis and in the investigation of porphyrin properties. Especially the synthesis of porphyrinic model systems to mimic the natural light harvesting systems in plants and bacterias is an very active and interesting field of porphyrin chemistry.[1)] Nearly all systems synthesized for those models bearing quinone groups as electron acceptor groups[2)] and only a few other electron acceptor groups were reported.[3)] Though the azo-group is a strong electron attracting moiety, there are no reports in the literature describing the use of this group as an electron acceptor group in porphyrin based model systems for natural photochemical reaction centers. This is mainly due to the more negative reduction potential of this group compared to quinone moieties thus making electron transfer processes from exited porphyrinic donors less favourable. Azobenzene and azobenzene derivatives are also well known optical switches which upon irradiation undergo *E/Z* isomerisation. During our studies directed towards the synthesis of model systems of photochemical reaction center chromophores, we became interested in the synthesis of azobenzene bridged diporphyrins. In these systems the interchromophoric distance and orientation can be varied by *E/Z* isomerisation of the connecting azobenzene spacer, thus giving rise to different spectroscopic and photochemical properties of the two isomers. We now report here the synthesis of new azobenzene bridged diporphyrins, where the azobenzene bridge is directly connected to the porphyrin macrocycles.

The synthesis of the new compounds is outlined in the scheme. To the best of our knowledge, this is the first reported synthesis of a diporphyrinic system where the azobenzene moiety is directly connected to the porphyrin chromophore. Some double decker porphyrins bridged by four azobenzene units recently were synthesized by Vögtle,[4)] but in these systems the azobenzene moiety is connected via an amide bridge to the para position of a TPP (*meso*-tetraphenylporphyrin) system. The starting compounds **1a** and **1b** were easily pre-



pared by a standard procedure and converted to porphyrins **2a** and **2b**, respectively by a simple acid ind saponification procedure. Our first attemps to couple the amino functionalized porphyrins **2a** and **2b**, res vely, using tert-BuOK/O_2 according to Shinkai's method[5] totally failed. We only obtained the corresp nitro substituted porphyrin in nearly quantitative yield. The oxidative coupling of the amino groups was with freshly prepared MnO_2.[6] The diporphyrins **3a** and **3b** were obtained in the very good yield of 60% 63% respectively. The diporphyrins were purified by column chromatography and recrystallized from n nol/CH_2Cl_2. Metal complexes were prepared using standard procedures[7] and purified by column chroma phy.

The synthesized porphyrins have interesting spectroscopic properties. Compared with TTP (*t* tetratolylporphyrin) the porphyrinic absorption bands are broadened thus indicating a ground state inter of the azobenzene and porphyrin chromophore. The Soret absorption furthermore has a strong tailing on t edge of the absorption band. This may result from $n \rightarrow \pi^*$ absorption of the Z-azobenzene moiety. Besid porphyrin absorption bands **3a** and **3b** show relatively weak and broadened bands in the azobenzene π region between 305 and 320 nm. Broadened absorption bands are also observed in the zinc complexs **Z** and **Zn-3b**. The metal complexes show a weak and broadened band at 317 nm and also a tailing of the

absorption. These absorptions may be due to the $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ transitions of the *E*- and *Z*-azobenzene unit respectively. Compared to Zn-TTP the Zn-porphyrin absorption bands are only insignificantly (approx. 3 nm) red shifted. In the free base fluorescence spectrum only one peak is detected at 655 nm. The zinc complexes show emissions at 601 and emissions at 646 nm. From these spectroscopic data we obtained a singlet energy E_S of 1.91 eV for **3a** and **3b** and 2.01 eV for **Zn-3a** and **Zn-3b**. These values are in agreement with those reported for other tetraarylporphyrins and zinc-tetraarylporphyrins, respectively.[8)]

Although from the spectroscopic data it is not clear if the *E*- or *Z*-isomer or a mixture of the isomers of the diporphyrins is formed, we think that the *E*-isomer is formed in the synthesis due to thermodynamic reasons. On the other side, the strong tailing of the Soret absorption may be due to an underlying *Z*-azobenzene $n \rightarrow \pi^*$ absorption. An *E/Z* isomerisation of the azo moiety might be possible at least for the zinc complexes via an light induced electron transfer mechanism thus making this system interesting for applications in molecular based information storage technology. The photochemistry and electrochemistry of **3a,b** and **Zn-3a,b** are currently under investigation.

EXPERIMENTAL SECTION

NMR Spectra were obtained in $CDCl_3$ and recorded with a Varian XL 200 spectrometer. Chemical shift values were given in ppm relative to TMS. Coupling constants were given in Hertz. Mass spectra were measured with a VG-Analytical VG70:250 E instrument. Electronic spectra were recorded on a Kontron Uvikon 860 instrument. Fluorescence spectra were recorded on a SMC 210 instrument. Column chromatography was carried out with Merck silica gel mesh size 0.06 - 0.2 mm.

Synthesis of porphyrins

Synthesis of 5-(p-acetamidophenyl)-10,15-20-tri(p-methylphenyl)porphyrin (1a)

Compound **1a** was prepared from 4-methylbenzaldehyde, 4-acetamidobenzaldehyde and pyrrole using a standard procedure. 5.37 g (80 mmol) pyrrole were added to a refluxing solution of 7.21 g (60 mmol) 4-methylbenzaldehyde and 3.23 g (20 mmol) 4-acetamidobenzaldehyde in 1.5 l propionic acid. After complete addition of the pyrrole, the reaction mixture was refluxed for 1 h. The mixture was cooled, and left for 12 h at room temperature. A porphyrin mixture crystallized and was isolated by filtration. The propionic acid was removed by distillation and the residue filtered giving crystals of a porphyrin mixture. The combined porphyrinic fractions were dried at 100 °C in vacuum and chromatographed on a silica gel column (20 x 5 cm) with CH_2Cl_2 as eluent. The first fraction collected was tetratolylporphyrin. After isolation of tetratolylporphyrin 5% ethyl acetate was added to the eluent. The second fraction collected was compound **1a**. The isolated product was dried in vacuum at 100 °C.- Yield: 2.25g (16%).- ^{1}H-NMR ($CDCl_3$): δ = - 2.79 (br s, 2 H, NH), 2.32 (s, 3 H, acetamido-CH_3), 2.69 (s, 9 H, tolyl-CH_3), 7.53 (d, J = 7.6 Hz, 6 H, H_m), 7.83 (d , J = 8.6 Hz, 2 H, $H_{m'}$), 8.07 (d, J = 8.0 Hz, 6 H, H_o), 8.13 (d, J = 8.5 Hz, 2 H, $H_{o'}$), 8.84 (s, 8 H, H_β).- ^{13}C-NMR ($CDCl_3$): δ = 21.53 (q, tolyl-CH_3), 24.81 (q, acetamido-CH_3), 117.92 (d, $C_{m'}$), 118.00 (s, C_{meso}), 120.16 (s, C_{meso}), 127.39 (d, C_m), 131.00 (s, C_β), 134.49 (d, C_o), 135.05 (d, $C_{o'}$), 137.33 (s, C_p), 137.46 (s, $C_{p'}$) 138.18 (s, $C_{ipso'}$), 139.20 (s, C_{ipso}), 145.98 (br, C_α), 168.63 (s, C=O).- UV-Vis (CH_2Cl_2): λ (log ε) = 419 (5.388), 516 (3.974), 552 (3.743), 591 (3.436), 647 (3.398).- FAB-MS: m/e = 714 (M^+ + 1).

Synthesis of 5-(p-acetamidophenyl)-10,15,20-tri(p-isopropylpenyl)porphyrin (1b)

In a 2 l flask 1.67 g (11.25 mmol) 4-isopropylbenzaldehyde, 0.612 g (3.75 mmol) 4-acetamidobenzaldehyde and 1.01 g (15 mmol) pyrrole were dissolved in 1.5 l CH_2Cl_2. Then 3.42 g trifluoroacetic acid were added and the reaction mixture stirred for 1 h at room temperature. Then 2.77 g (11.25 mmol) o-chloranil were added and the mixture stirred for 1 h. Triethylamine (2.2 ml) was added and the solvent evaporated. The remaining residue was chromatographed on a silica gel column with CH_2Cl_2/ethyl acetate (10:1 v:v) as eluent. A porphyrinic fraction was collected and chromatographed on a second column with CH_2Cl_2 as eluent. The first fraction collected was tetra(p-isopropylphenyl)porphyrin, the second one was the expected product **1b**.

Tetra(p-isopropylphenyl)porphyrin: Yield: 368 mg (17%).- ^{1}H-NMR ($CDCl_3$): δ = -2.78 (br s, 2 H, NH), 1.59 (d, J = 6.8 Hz, 24 H, $-CH_3$), 3.26 (sept, J = 6.8 Hz, 4 H, CH), 7.60 (d, J = 7.8 Hz, 8 H, H_m), 8.14 (d, J = 7.8 Hz, 8 H, H_o), 8.87 (s, 8 H, H_β).- ^{13}C-NMR ($CDCl_3$): δ = 24.30 (q, $-CH_3$), 34.11 (d, -CH), 120.12 (s, C_{meso}), 124.73 (d, C_m), 131,00 (s, C_β), 134.70 (d, C_o), 139.60 (s, C_{ipso}), 148.14 (s, C_p).- UV-Vis (CH_2Cl_2): λ (log ε) = 418.5 (5.598), 516.4 (4.226), 552.0 (3.996), 591.6 (3.695), 648.8 (3.630).- FAB-MS: m/e = 782 (M^+).- Anal. Calc. for $C_{56}H_{54}N_4$ (783.07): C 85.89 H 6.95 N 7.15. Found: C 85.97 H 7.02 N 7.22.

1b: Yield: 568 mg (19%).- ^{1}H-NMR ($CDCl_3$): δ = -2.74 (br s, 2 H, NH), 1.54 (d, J = 7.4 Hz, 18 H, $-CH_3$), 2.34 (s, 3 H, $-CO-CH_3$), 3.26 (sept, J = 7.4 Hz, 3 H, -CH), 4.14 (br s, 1 H, -CO-NH-), 7.59 (d, J = 8.2 Hz, 6 H, H_o), 7.85 (d, J = 8.4 Hz, 2 H, $H_{m'}$), 8.12 (d, J = 7.8 Hz, 6 H, H_m), 8.10 (d, J = 8.4 Hz, 2 H, $H_{o'}$) 8.85 (AB, 4 H, $H_{\beta'}$), 8.87 (s, 4 H, H_β).- ^{13}C-NMR ($CDCl_3$): δ = 24.30 (q, $-CH_3$), 24.89 (q, $-COCH_3$), 34.11 (d, -CH), 117.91 (d, $C_{m'}$), 119,08 (s, C_{meso}), 120.28 (s, C_{meso}), 124.73 (d, C_m), 130.96 (d, C_β), 134.69 (d, C_o), 135.14 (d, $C_{o'}$), 137.47 (s, $C_{ipso'}$), 138.26 (s, $C_{p'}$), 139.50 (s, C_p), 146,58 (br, C_α), 148.01 (s, C_{ipso}), 168.52 (s, CO).- UV-Vis (CH_2Cl_2): λ (log ε) = 419.1 (5.595), 516.4 (4.224), 552.3 (4.006), 591.9 (3.690), 648.6 (3.688).- FAB-MS: m/e = 798 (M^+ + 1).- Anal. Calc. for $C_{55}H_{51}N_5O$ (798.05): C 82.78 H 6.44 N 8.78. Found: C 81.53 H 6.44 N 8.93.

Synthesis of 5-(p-aminophenyl)-10,15,20-tri(p-methylphenyl)porphyrin (2a)

A suspension of 280 mg (0.39 mmol) **1a** was refluxed for 5h in 20 % HCl. The solution was cooled and neutralized carefully by adding 10% KOH solution. The neutralized solution was extracted 5 times with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on a silica gel column (5 x 20 cm) using CH_2Cl_2 as eluent.

Yield: 230 mg (88%).- ^{1}H-NMR ($CDCl_3$): δ = -2.76 (br s, 2 H, NH), 2.70 (s, 9 H, aryl-CH_3), 3.98 (br s, 2 H, NH_2), 7.03 (d, J = 8.4 Hz, 2 H, $H_{o'}$), 7.54 (d, J = 7.8 Hz, 6 H, H_m), 7.78 (d, J = 8.4 Hz, 2 H, $H_{m'}$), 8.09 (d, J = 8.0 Hz, 6 H, H_o), 8.85 (s, 4 H, H_β), 8.88 (AB, 4 H, J = 4.9 Hz, $H_{\beta'}$).- ^{13}C-NMR ($CDCl_3$): δ = 21.55 (q, aryl-CH_3), 113.43 (d, $C_{m'}$), 119.77 (s, C_{meso}), 119.96 (s, C_{meso}), 120.50 (s, C_{meso}), 127.38 (d, C_m), 130.84 (br s, C_β), 132.53 (s, $C_{ipso'}$), 134.51 (d, C_o), 135.68 (d, $C_{o'}$), 137.26 (s, C_{ipso}), 139.34 (s, C_p), 145.92 (s, $C_{p'}$).- UV-Vis (CH_2Cl_2): λ (log ε) = 420 (5.515), 518 (4.252), 555 (4.070), 593 (3.732), 649 (3.73).- FAB-MS: m/e = 672 (M^+).- Anal Calc. for $C_{47}H_{37}N_5 \cdot H_2O$ (689.87): C 81.83, H 5.70 N 10.15. Found: C 82.03 H 5.51 N 10.31.

Synthesis of 5-(p-aminophenyl)-10,15,20-(p-isopropylphenyl)porphyrin (2b)

220 mg (0.25 mmol) **1b** were treated as described for the synthesis of **2a**. Yield: 165 mg (87%) ^{1}H-NMR ($CDCl_3$): δ = -2.74 (br s, 2 H, NH), 1.54 (d, J = 6.8 Hz, 18 H, $-CH_3$), 3.25 (sept, J = 6.8 Hz, 3 H, -CH), 3.98 (br s, 2 H, $-NH_2$), 7.04 (d, J = 8.4 Hz, 2 H, $H_{m'}$), 7.59 (d, J = 7.8 Hz, 6 H, H_o), 7.99 (d, J = 8.4 Hz, 2 H, $H_{o'}$), 8.13 (d, J = 7.8 Hz, 6 H, H_m), 8.86 (s, 4 H, H_β), 8.90 (AB, 4 H, $H_{\beta'}$).- ^{13}C-NMR ($CDCl_3$): δ = 24.30 (q, $-CH_3$), 34.11 (d, -CH), 113.43 (d, $C_{m'}$), 119.90 (s, C_{meso}), 120.06 (s, C_{meso}), 120.47 (s, C_{meso}), 124.73 (d, C_m), 130.88 (d, C_β), 131.17 (s, $C_{ipso'}$), 134.70 (d, C_o), 135.74 (d, $C_{o'}$), 139.62 (s, C_{ipso}), 145.90 (s, $C_{p'}$), 147.91 (br, C_α), 148.11 (s, C_p).- UV-Vis (CH_2Cl_2): λ (log ε) = 419.4 (5.545), 516.3 (4.164), 552.5 (3.945), 591.5 (3.655), 648.0 (3.636).- FAB-MS: m/e = 757 (M^+ + 1).- Anal. Calc. for $C_{59}H_{49}N_5$ (756.02): C 84.20 H 6.53 N 9.26. Found: C 84.29 H 6.59 N 9.33.

Synthesis of 4,4'-bis[5-(10,15,20-tri(p-tolyl))porphyrinyl]azobenzene (3a)

2 g freshly prepared MnO_2 were added to a solution of 100 mg (0.149 mmol) **2a** in 25 ml $CHCl_3$. The reaction mixture was refluxed for 7h. The reaction mixture was filtered, and the residue washed 3 times with 5 ml $CHCl_3$. The solution was dried over $MgSO_4$ and the solvent evaporated. The remaining solid was chromatographed on a silica gel column (20 x 5 cm) with $CHCl_3$ as eluent.

Yield: 60 mg (60 %).- ^{1}H-NMR ($CDCl_3$): δ = -2.77 (br s, 4 H, NH), 2.71 (s, 18 H, aryl-CH_3), 7.50 (d, J = 7.8 Hz, 12 H, H_m), 8.05 (d, J = 7.8 Hz, 12 H, H_o), 8.40 (s, 8 H, azo-aryl-H), 8.80 (s, 8 H, H_β), 8.88 (AB, J = 6.0 Hz, 8 H, $H_{\beta'}$).- UV-Vis (CH_2Cl_2): λ (log ε) = 305 (4.56), 420 (5.84), 517 (4.65), 555 (4.48), 592 (4.103), 648 (4.10) nm. Fluorescence (CH_2Cl_2): λ = 653 nm (Exitation: 419 nm).- FAB-MS: m/e = 1338 (M^+, 40 %), 687 (35 %), 657 (100 %).- Anal. Calc. for $C_{94}H_{70}N_{10} \cdot H_2O$ (1357.69): C 83.16 H 5.35 N 10.31. Found: C 83.26 H 5.94 N 10.42.

Synthesis of Zn-3a:

10 mg (7.5 10^{-3} mmol) **3a** were added to a solution of 2 g $Zn(COOCH_3)_2$ in methanol/$CHCl_3$ (1:5) and refluxed for 3 h. Then 50 ml water were added, the organic layer separated and washed 3 times with 10 ml of water. The organic layer was dried ($MgSO_4$) and the solvent evaporated. The residue was chromatographed on a silica gel column (20 x 1.5 cm) with $CHCl_3$ as eluent.

Yield 9 mg (86 %).- UV-Vis (CH_2Cl_2): λ = 317, 425, 465, 557, 599 nm.- Fluorescence (CH_2Cl_2): λ = 601, 646 nm.

Synthesis of bis[5-(10,15,20-tri(p-isopropylphenyl)porphyrinyl]azobenzene (3b)

105 mg (0.139 mmol) of **2b** was treated in the same manner as described for the synthesis of **3a** from **2a**. Yield: 66 mg (63%).- ^{1}H-NMR ($CDCl_3$): δ = -2.70 (br s, 4 H, -NH), 1.56 (d, J = 6.8 Hz, 36 H, -CH_3), 3.28 (sept, J = 6.8 Hz, 6 H, -CH), 7.63 (d, J = 6.4 Hz, 12 H, H_m), 8.16 (d, J = 6.4 Hz, 12 H, H_o), 8.49 (s, 8 H, azo-aryl-H), 8.90 (s, 8 H, H_β), 8.97 (s, 8 H, $H_{\beta'}$).- UV-Vis (CH_2Cl_2): λ (log ε) = 305.0, 420.3, 518.1, 554.7, 593.0, 650.2.- Fluorescence (CH_2Cl_2): λ = 653 nm (Exitation: 419 nm).- FAB-MS: m/e = 1507 (M^+).- Anal. Calc. for $C_{106}H_{94}N_{10}$ (1508.00): C 84.43 H 6.28 N 9.29. Found C 84.29 H 6.46 N 9.24.

Synthesis of Zn-3b:

Synthesis of **Zn-3b** was performed as described for **Zn-3a**. 21 mg **3b** were reacted. Yield: 17 mg (75%). UV-Vis (CH_2Cl_2): λ (log ε) = 317 (4.660), 421.3 (4.904), 553.2 (4.272), 593.2 (4.214) nm.- Fluorescence (CH_2Cl_2): 601, 646 nm.

Acknowledgement: Support of this research by the Deutsche Forschungsgemeinschaft (DFG), the Fonds der Chemischen Industrie (FCI), IBM Deutschland GmbH and Siemens AG is gratefully acknowledged.

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