

Pergamon

0040-4039(95)02405-0

## Synthesis and Structural Characterization of Nonplanar Tetraphenylporphyrins with Graded Degree of β-Ethyl Substitution

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Abstract: Tetraphenylporphyrins bearing two, four, and six  $\beta$ -ethyl groups have been synthesized by mixed condensation of benzaldehyde with diethylpyrrole and pyrrole. Investigation of all isomers by spectroscopy and X-ray crystallography shows a series of porphyrins with graded degree of nonplanarity depending on number and position of the ethyl substituents.

Nonplanar porphyrins with distortions of the macrocycle resulting from steric hindrance at the periphery have become a focus of attention with the suggestion that conformational distortion may serve to fine-tune the physical porperties of tetrapyrrole chromophores<sup>1</sup> One of the most widely studied nonplanar porphyrins is octaethyltetraphenylporphyrin  $3^2$ , the structural hybrid of the planar octaethyl-1 and tetraphenylporphyrin (TPP) 2. Compound 3 and related dodecasubstituted porphyrins exhibit a severe nonplanar saddle conformation with out-of-plane displacements of the  $\beta$ -pyrrole atoms of more than 1 Å.<sup>2,3</sup> While a large body of structural information is available for both planar 1 and  $2^4$  and now for the very nonplanar 3, there remains a "conformational gap" of the intervening compounds 4 - 7 with intermediate degree of  $\beta$ -ethyl substitution. Clearly, a series of porphyrins with graded degree of conformational distortion should be very interesting for studying the effect of nonplanarity on the physicochemical properties of the porphyrin macrocycle. While some attempts have been made to prepare related series of porphyrins with varying degree of nonplanarity,<sup>5</sup> only fragmentary structural information is yet available.



We have synthesized the complete "homologous" series 2 - 7 by mixed condensation of pyrrole, 3,4diethylpyrrole and benzaldehyde. An equimolar solution of pyrrole and diethylpyrrole (0.01 mol, each) and



benzaldehyde (0.02 mol) was dissolved in 2 1  $CH_2Cl_2$  and treated with BF<sub>3</sub>OEt<sub>2</sub> (0.002 mol) for 2 h. In situ oxidation of the porphyrinogens with 4 equiv. DDQ<sup>6</sup> yielded a mixture of all 6 possible compounds. The porphyrins were isolated by first separating the mixture in 3 fractions on silica gel, eluting with  $CH_2Cl_2$  and increasing concentrations of methanol. The first fraction, containing 2 and 4, was separated by chromatography on grade III aluminium oxide, eluting with toluene/n-hexane (1:1). The second fraction, containing 5 and 6, was separated on aluminium oxide eluting with toluene containing 1-5 % methanol. The remaining fraction, containing 7 and 3, could not be separated directly. Rather, the free base mixture was converted to the corresponding iron(III) derivatives, which were separated by chromatography on aluminium oxide eluting with 1 % NEt<sub>3</sub> in toluene; removal of the metal then yielded 7 and 3.<sup>7</sup>

Porphyrin	λmax (nm)				
2	418	515	547	590	645
4	420	521	555	591	645
5	426	527		593	649
6	433	540	575	606	672
7	444	544	588	623	683
3	446	548	588	634	686

Table I UV/vis absorption maxima (in CH<sub>2</sub>Cl<sub>2</sub> + 1 % NEt<sub>3</sub>) for the porphyrins studied.

Visible absorption spectra (Table I) of all isomers show an increasing bathochromic shift of the absorption bands in the order  $2 \le 4 \le 5 \le 6 \le 7 \le 3$ . A direct correlation between red-shift of absorption bands and macrocycle distortion has been shown for all sterically strained porphyrins.<sup>1</sup> Increasing nonplanarity in solution is also shown by increasing deshielding of the NH-protons in the <sup>1</sup>H-NMR spectrum.<sup>7</sup> Nevertheless, unambiguous proof of the macrocycle conformation can only be obtained by X-ray crystallography. We have therefore determined the crystal structures of all four new compounds (Fig. 1).<sup>8</sup> The average deviation of the macrocycle atoms from planarity increases in the order 4 (0.10 Å), 5 (0.29 Å), 6 (0.38 Å) and 7 (0.46 Å) and this correlates well with the spectroscopic data for the solution conformation. While the diethyl derivative 4 shows only moderate deviations from planarity for some  $\beta$ -pyrrole positions, increasing saddle-type displacement patterns are found in 5 - 7. The symmetric tetraethyl derivative 5 exhibits a symmetric saddle conformation. Interestingly, chair-type conformation found in the crystal structures of 2,3,12,13-tetrachloro/bromothe tetramesitylporphyrin,<sup>5b</sup> with a lesser degree of nonplanarity than found in 4, is not realized in 5. Indeed, the only crystallographically **B-phenyl-TPP** series, 5c studied trans-isomer of the related



Fig. 1 Molecular structures of 4 - 7. Numbers give the deviations of the macrocycle atoms from the 4N-plane (in pm).

trans-tetraphenyl TPP, was found to be planar.<sup>9</sup> In 4, 6, and 7 the distortion mode is asymmetric and individual  $\beta$ -pyrrole displacements in 6 and 7 are in the range observed for dodecasubstituted derivatives.<sup>2,3</sup> As expected, larger displacements are typically found close to  $\beta$ -ethyl-meso-phenyl groups whereas smaller displacements are observed in parts of the molecule bearing  $\beta$ -pyrrole hydrogens, also explaining the higher degree of distortion in 6 with the ethyl groups flanking the C5-meso-phenyl, compared to 5. Nevertheless, a certain amount of redistribution of the steric strain occurs, as evidenced by the still significant displacements in 4 -7 for pyrrole carbons with  $\beta$ -hydrogens.

These results indicate that the present  $\beta$ -ethyl-TPP series, with their stepwise increase in nonplanarity, will be a good candidate for studying the effects of gradual increases in macrocycle distortions on the porphyrin properties. Studies on the synthesis and structural chemistry of related metal complexes and investigations of the electrochemistry and photophysics are currently under way and will be reported in due course. Acknowledgement. This work was supported by the Deutsche Forschungsgemeinschaft (Se543/2-1 and /2-2) and the Fonds der chemischen Industrie. We are indebted to Professor K.M. Smith for providing instrument time at the UC Davis crystallographic facility.

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- 7. Yields (%, unoptimized) are: 2: 16.8, 4: 14.4, 5: 1.65, 6: 12.1, 7: 9.8, 3: 18.1. <sup>1</sup>H NMR CDCl<sub>3</sub>, RT), m.p., and mass spectrometric data are as follows: 4: <sup>1</sup>H NMR: (500 MHz) δ -3.04 (s, 1H, NH), -2.45 (s, 1H, NH), 1.00 (t, 6H, J = 7 Hz, CH<sub>3</sub>), 2.85 (br s, 4H, CH<sub>2</sub>), 7.72 (m, 12H, arom. H<sub>m</sub>, H<sub>p</sub>), 8.20 (m, 8H, arom. H<sub>o</sub>), 8.56 (d, 2H, J = 5 Hz, H-7, H-18), 8.67 (d, 2 H, J = 5 Hz, H-8, H -17), 8.94 (s, 2 H, H-12, H-13); HRMS: calc. 670.30965, found 670.30926; m.p. 324-325 °C. 5: <sup>1</sup>H NMR: (500 MHz) δ -2.60 (s, 2H, NH), 0.86 (t, 12H, J = 7 Hz, CH<sub>3</sub>), 2.81 (q, 8H, J = 7Hz, CH<sub>2</sub>), 7.66-7.78 (m, 12 H, arom. H<sub>p</sub>, H<sub>m</sub>), 8.21 (m, 8H, arom. H<sub>o</sub>), 8.30 (s, 4H, β-pyrrole); HRMS: calc. 726.37225, found 726.37293; m.p. 296-298 °C. 6: <sup>1</sup>H NMR: (250 MHz) δ -2.38 (br s, 2H, NH), 0.46 (m, 6H, CH<sub>3</sub>), 0.68 (t, 6H, J = 7Hz, CH<sub>3</sub>), 2.36 (br s, 4H, CH<sub>2</sub>), 2.56 (br s, 4H, CH<sub>2</sub>), 7.74 (m, 12 H, arom. H<sub>p</sub>, H<sub>m</sub>), 8.36 (m, 8H, arom. H<sub>o</sub>), 8.30 (s, 4H, β-pyrrole); HRMS: calc. 726.37225, found 726.37211; m.p. 315-316 °C. 7: <sup>1</sup>H NMR: (500 MHz) δ -2.23 (br s, 2H, NH), 0.35 (m, 6H, CH<sub>3</sub>), 0.68 (m, 6H, CH<sub>3</sub>), 1.3-2.8 (m, 12H, CH<sub>2</sub>), 7.65 (m, 12 H, arom. H<sub>p</sub>, H<sub>m</sub>), 8.25 (m, 10H, arom. H<sub>o</sub>, β-pyrrole); HRMS: calc. 782.43485, found 782.43436; m.p. 295-297 °C.
- 8. Crystal data: 4: monoclinic, Cc, a = 18.333(6) Å, b = 20.664(14) Å, c = 10.180(11) Å,  $\beta$  = 109.65(5)°, V = 3632(4) Å<sup>3</sup>, Z = 4, ref. F<sup>2</sup>, R<sub>1</sub> (I>2 $\sigma$ (I)) = 0.0515, wR2 = 0.1374; 5: monoclinic, P2<sub>1</sub>/c, a = 13.531(6) Å, b = 28.172(11) Å, c = 12.184(4) Å,  $\beta$  = 112.55(3)°, V = 4289(3) Å<sup>3</sup>, Z = 4, R<sub>1</sub> = 0.1157, wR2 = 0.2641; 6: monoclinic, P2<sub>1</sub>/c, a = 16.992(5) Å, b = 16.206(3) Å, c = 17.247(6) Å,  $\beta$  = 115.66(2)°, V = 4281(2) Å<sup>3</sup>, Z = 4, ref. F<sup>2</sup>, R<sub>1</sub> = 0.0675, wR2 = 0.1675; 7: monoclinic, P2<sub>1</sub>/n, a = 11.274(4) Å, b = 17.186(7) Å, c = 25.339(9) Å,  $\beta$  = 98.51(3)°, V = 4856(3) Å<sup>3</sup>, Z = 4, R<sub>1</sub> = 0.0859, wR2 = 0.2241. Further details on the structure determinations of the free bases and related metal complexes will be given elsewhere.
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(Received in Germany 5 September 1995; accepted 14 December 1995)