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One-pot Synthesis of Strapped Porphyrins and Face-to-face Dimeric Porphyrins

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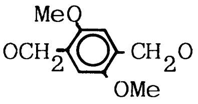
Strapped porphyrins were prepared directly by the acid-catalyzed condensation of 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane with methylenedioxy bridged dialdehydes with bridging carbon atoms longer than 5. With dialdehydes having shorter chains, face-to-face dimeric porphyrins were obtained. In short chain strapped porphyrins, distortion of porphyrin ring is confirmed by their ^{1}H-NMR data, red shifted absorption, and fluorescence spectra.

In relation to the importance of porphyrin ring-distortion in biological functions of hemoproteins and photosynthetic pigments, considerable attention has been focused on the synthesis and characterization of permanently distorted porphyrins.[1)] Among these, extremely short-chain strapped porphyrins are very simple and useful for this model.[2)] Recently we have found that 5,15-diaryl-octaalkylporphyrin can be prepared in high yields in a one-pot procedure without separation of the porphyrinogen intermediate.[3)] Described herein is the direct synthesis of strapped porphyrins based on our improved method.

Strapped porphyrins synthesized here are 5,15-diphenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine derivatives in which ortho positions of the meso-phenyl groups are bridged by an alkoxy chain with carbon atoms longer than 5.[4)] General procedure is as follows: 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane 1[5)] (100 mg, 0.43 mmol) and the dialdehyde 2[6)] (0.22 mmol) were dissolved or suspended in dry acetonitrile under N_2, and to this mixture a catalytic amount of trichloroacetic acid (100 mg) was added. After standing at room temperature for about 5 hours, p-chloranil (0.3 g, 1.2 mmol) in dry tetrahydrofuran (THF, 10 ml) was added and the mixture was stirred overnight. Porphyrin product was separated on alumina column (activity Ⅲ) eluting with CH_2Cl_2, and recrystallized from CH_2Cl_2-methanol (Table 1).[7,8)] The cyclization yields were found to be dependent on the concentrations of the reactants (Table 1, Runs 1-4). The highest yield (15%) was obtained at [1]=0.02 M (1 M=1 mol dm^{-3}). At high concentrations [1] > 0.05 M, the formation of the dark blue insoluble solids took place predominantly, while at low concentrations [1] < 0.01 M, the yields decreased significantly.

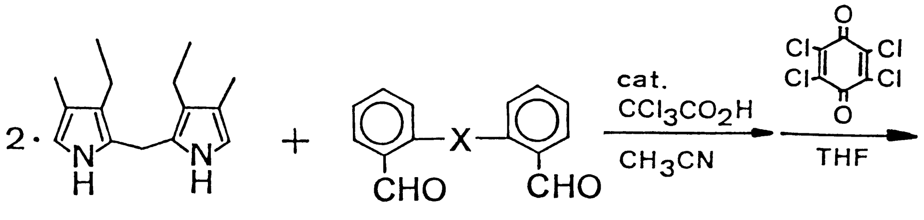
In the cases of dialdehydes 2d and 2e, the corresponding strapped porphyrins were no longer formed but instead face-to-face porphyrin dimers 4d and 4e

Table 1.

Run	Dialdehyde	X	Conc. 1 /M	Product	Yield/%	m/z[b)]
1	2a	$O(CH_2)_5O$	0.05	3a	6	731
2	2a	$O(CH_2)_5O$	0.03	3a	13	
3	2a	$O(CH_2)_5O$	0.02	3a	15	
4	2a	$O(CH_2)_5O$	0.01	3a	trace	
5	2b	$O(CH_2)_{10}O$	0.02	3b	21	801
6	2c	$O(CH_2)_6O$	0.02	3c	25	745
7	2d	$O(CH_2)_4O$	0.02	4d	5[a)]	1558-1563[a)]
8	2e	$O(CH_2)_3O$	0.02	4e	2[a)]	1530-1535[a)]
9	2f	$CO_2(CH_2)_{10}O_2C$	0.02	3f	33	857
10	2g		0.02	3g	54	765
11	2h		0.03	3h	61	825

a) Purified as bis-Zinc complexes.

b) FAB-Mass spectra (M+H$^+$).



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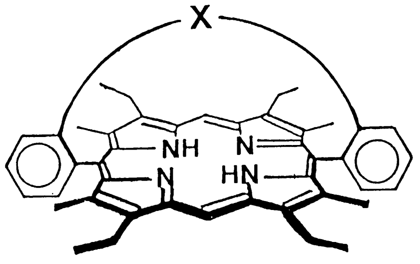

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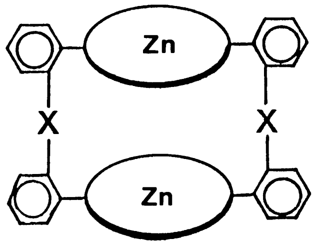

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Table 2. Physical Properties of the Strapped Porphyrins

	δ / ppm in $CDCl_3$			λ max / nm in CH_2Cl_2	
Compd.	X	meso-H	NH	Soret	Q-bands
3f	3.31, -0.28, -0.83, -1.05, -1.18	10.16	-2.19	411	509 541 580 629
3b	3.68, 0.55, -0.94, -0.94, -1.69	10.16	-2.33	409	507 539 575 629
3c	2.29, -1.85, -2.85	9.93	-1.70	412	510 543 579 632
3a	0.96, -1.70, -3.49	9.79	-1.27	417	516 552 587 637
3g	2.92(s, OCH_2), 3.42(s, Ar-H)	9.74	-1.36	415	514 550 584 637
3h	3.47, 2.44(each d, J=13Hz, OCH_2) 3.50(s, Ar-H), 1.86(s, OCH_3)	9.76	-2.52	417	514 550 585 639
5[a)]		10.22	-2.40	407	507 536 574 622

a) 5, 15-Diphenyl-2, 8, 12, 18-tetraethyl-3, 7, 13, 17-tetramethylporphine was used as a reference.

were obtained in 5% and 2%, respectively (Table 1, Runs 7, 8).[9)] Although the yields of 4d and 4e are not so high, this reaction will be useful for the preparation of porphyrin dimers of this type in view of its simple manupulation, easy separation, and direct synthesis from easily available starting materials.

Strapped porphyrins 3g and 3h, in which the strap linkages contain aromatic ring, were also prepared by this procedure in high yields (Table 1, Runs 10, 11). From the CPK (Corey-Pauling-Koltun) models of 3g and 3h, it is suggested that the porphyrin ring of 3g and 3h is forced to be distorted due to the short p-xylylene linkages. However, the p-xylylene linkages are best-fitted in length for its porphyrinogen precursor. Probably this situation may account for the high yields of 3g and 3h.

In their ^{1}H-NMR spectra of strapped porphyrins, the protons in the strap were significantly upfield-shifted in accord with these protons lying above the porphyrin plane (Table 2). On shortening the strap linkage, the porphyrin ring was forced to be increasingly distorted from planarity, which was realized by the systematic decrease of porphyrin ring current shielding for the meso-H and inner NH protons as well as the red-shifts of Soret and Q-bands (Table 2).[10)] Based on these decreased ring current effect, it may be concluded that the distortion enforced on the porphyrins 3a, 3g, and 3h diminished the aromaticity of the porphyrin π system. Finally, it is worth mentioning that even the relative fluorescence quantum yield and fluorescence lifetime were significantly perturbed by the ring-distortion in the most distorted porphyrin 3a; its relative fluorescence quantum yield to the reference porphyrin 5 was ca. 0.6 and its fluorescence lifetime was 5.9 ns.

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4) Stepwise synthesis for this type of strapped porphyrin was reported: J. E. Baldwin, M. J. Crossley, T. Klose, E. A. O'rear III, and M. K. Peters, Tetrahedron, 38, 27(1982).

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6) Dialdehydes 2 were prepared according to the published procedure.[2a)]

7) All new compounds described in this paper gave satisfactory spectral data consistent with the assigned structure.

8) Small amounts (1-2%) of porphyrin dimers (4a, 4b, 4c, 4f, 4g, 4h) were obtained from the filtrate on further purification.

9) The ^{1}H-NMR spectrum of bis-zinc dimer 4d was broadened and complicated at ambient temperatures. On heating the sample to 100 ℃ in 1,1,2,2-tetrachloroethane-d_2, the spectrum became sharp and the peak assignment was achieved. 4d: ^{1}H-NMR($CDCl_2CDCl_2$, at 100 ℃) 9.67(s, meso-H), 7.64, 7.25-7.14 (each m, Ar-H), 3.73(m, β-$\underline{CH_2}CH_3$), 3.42(br, OCH_2), 2.31(s, β-CH_3), 1.56(t, β-$CH_2\underline{CH_3}$), 0.49(br, $OCH_2\underline{CH_2}$); MS (FAB, in m-nitrobenzyl alcohol matrix, 1.5 eV) m/z 1558-1563(M^+); UV-vis (CH_2Cl_2) 408, 538, and 574 nm.

10) The red shifts of Soret and Q-bands in distorted porphyrins were reported in Ref. 2.

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