

## Isomeric Double Decker Porphyrins Bridged by Four Azobenzene Units

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A novel macropentacyclic system (**1**) containing double layered porphyrin units which are bridged by four azobenzene links has been synthesized, two stable isomers being isolated, differing in spatial arrangement of the amide groups and azobenzene links; the complex formation of these compounds with zinc(II) is reported.

In an attempt to combine two fields of topical organic chemistry in one molecule, namely 'large molecular cavities'<sup>1</sup> and 'optical switches',<sup>2</sup> we designed the dimeric porphyrin (**1**) containing four azobenzene bridges. Under irradiation the azo groups should undergo *E/Z* isomerization and by this the size and shape of the molecular cavity should be modified.

To overcome the problems of connecting four amide bonds between two molecules in a macrocyclization reaction, we developed the following new concept: a rigid spacer group [like *meso*-tetra( $\alpha,\alpha,\alpha,\alpha$ -*o*-aminophenyl)porphyrin (**2**)]<sup>3</sup> bearing all-*cis* predirected functions ( $-\text{NH}_2$ ) is connected with four chains of low flexibility (azobenzene-dicarboxylic acid units) so that an intermediate (**5**) with favourably directed links will arise, which finally is treated with a second identical spacer (**2**) to obtain the macropentacyclic species (**1**).<sup>4</sup>

The synthesis started with the preparation of the porphyrin (**2**) and after equilibration to the  $\alpha,\alpha,\alpha,\alpha$ -atropisomer<sup>7,8</sup> it was coupled with the azobenzene (**10**) to give the porphyrin tetraester (**3**)<sup>†</sup> in 80% yield. The one-side protected acid chloride (**10**) was prepared from (**6**),<sup>9</sup> by treatment first with  $\text{PCl}_5$  in  $\text{CHCl}_3$  to give (**7**) and secondly with ethanol in order to get the diester (**8**).<sup>10</sup> Saponification of only one ester group of this species with  $\text{KOH}/\text{EtOH}$  and subsequent reaction with  $\text{PCl}_5/\text{CHCl}_3$  gave (**10**).<sup>†</sup> The ester functions of the tetra-linked porphyrin (**3**) were saponified with  $\text{KOH}/\text{EtOH}$  tetrahydrofuran (THF)<sup>11</sup> to get the tetra-potassium salt of the tetra-linked porphyrin (**4**) in 98% yield. Reaction of (**4**) with  $\text{SOCl}_2$  gave the porphyrin tetra-acid chloride (**5**) which was used for cyclization without further purification.<sup>12</sup> To prevent polycondensation the cyclization of compounds (**2**) and (**5**) was carried out under high dilution conditions in  $\text{THF}/\text{Et}_3\text{N}$  in such a manner that a final concentration of  $1.8 \times 10^{-3} \text{ M}$  was reached.

After two-fold chromatography on silica gel, eluting the first column with  $\text{CHCl}_3/\text{acetone}$  (40:3) and the second with

$\text{CH}_2\text{Cl}_2/\text{CHCl}_3/\text{acetone}$  (10:10:1), two structural isomers (**1a**)<sup>†</sup> and (**1b**)<sup>†</sup> of the fourfold bridged porphyrin dimer were isolated.

Final extraction of impurities with boiling ether gave (**1a**) in 12% and (**1b**) in 6% overall yield. The structural assignment of (**1a**) and (**1b**) is based on fast atom bombardment (FAB) mass spectroscopy [(**1a**):  $M^+ + \text{H}$ , 2285.79; (**1b**):  $M^+ + \text{H}$ , 2285.78; for  $\text{C}_{144}\text{H}_{93}\text{N}_{24}\text{O}_8$  calc. 2285.76],  $^1\text{H}$  n.m.r., and u.v.-visible spectra.

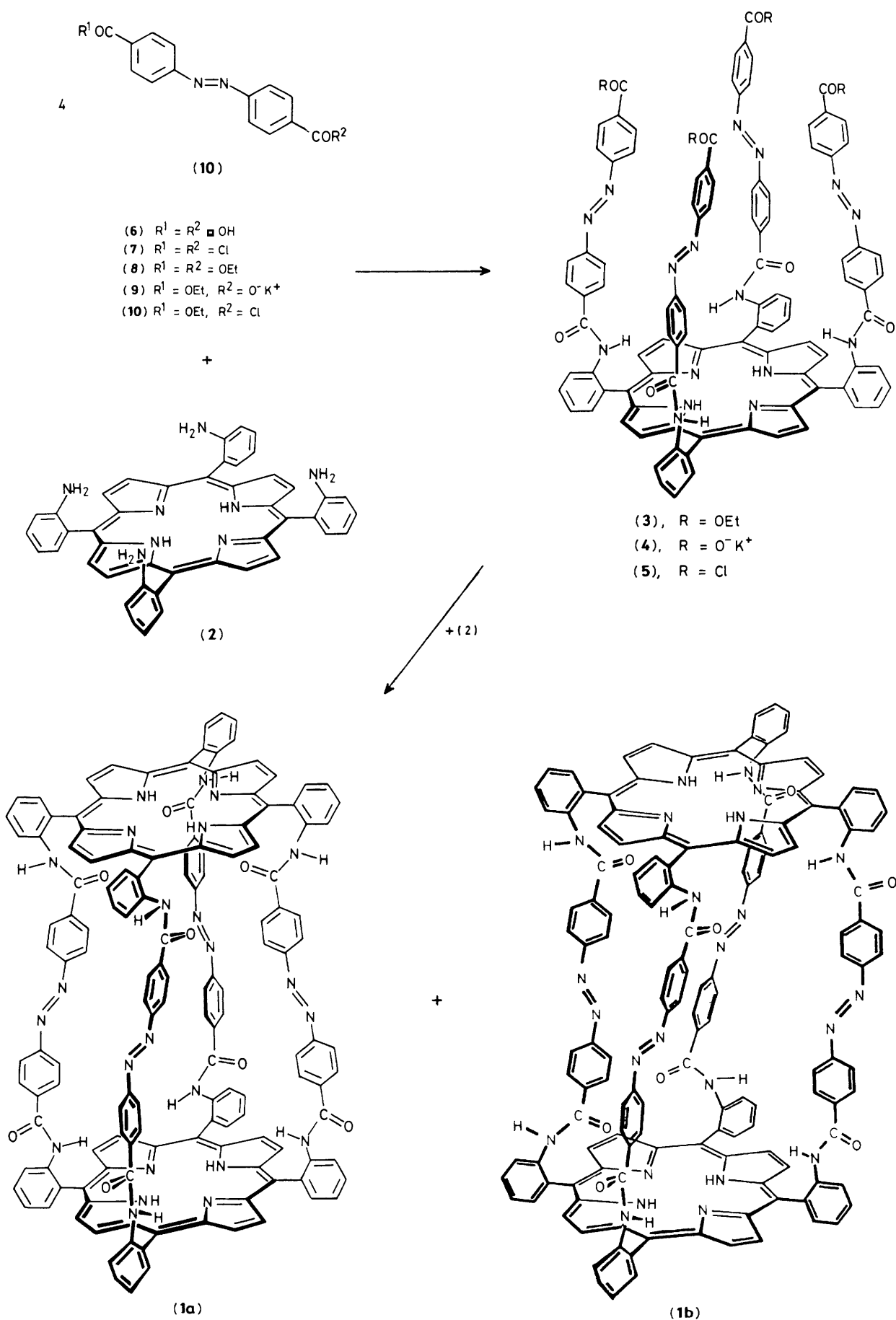
The  $^1\text{H}$  n.m.r. spectra of (**1a**) show a set of 4 NH-protons at  $\delta -2.8$  indicating only a slight interaction of the two porphyrin systems. Two AA'BB' resonances at  $\delta$  5.51, 5.92 and  $\delta$  7.05, 7.61, each integrating for 16 H, are due to four *E*-azobenzene groups.

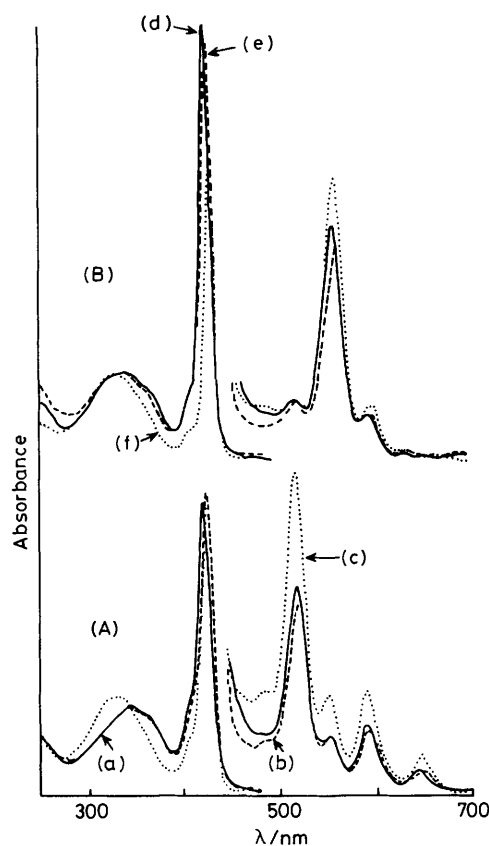
The amide protons identified by H/D exchange gave two signals at  $\delta$  9.17 and  $\delta$  10.78, each integrating for four protons. Because of the big difference of 1.61 p.p.m. between the two signals and the fact that in the Zn complex only the signal at  $\delta$  9.17 p.p.m. is upfield shifted we suppose that one set of amide H atoms is directed into the cavity and the other set out of the cavity, so that the symmetrical structure (**1a**) results. The  $^1\text{H}$  n.m.r. of (**1a**) is also in good agreement with the least strained Corey-Pauling-Koltun (CPK) model structure.

The isomer (**1b**) in contrast to (**1a**) shows some different signals in the same regions. A signal of 4 NH protons at  $\delta -3$  is slightly upfield shifted compared to (**1a**). Two AA'BB' systems at  $\delta$  5.38, 6.12 and  $\delta$  6.75, 6.97 p.p.m. show an intensity corresponding to 8 protons each. The signals of the remaining 16 azobenzene protons are covered by other signals in the complex region between  $\delta$  7.1 and 8.5.

In (**1b**) the amide protons show four signals at  $\delta$  9.12, 9.40, 10.31, and at  $\delta$  10.57, each integrating for 2 protons (identified by H/D exchange). These results are indicative of a structure for (**1b**) in which the left-hand and the frontal amide protons of the upper porphyrin are directed outwards and the backside and right amide protons are directed into the cavity; the left-hand and backside protons of the lower porphyrin are orientated outwards and right and frontal amide protons into the macrocycle.

<sup>†</sup> The new compounds gave satisfactory spectroscopic, analytical and mass spectral data.





**Figure 1.** U.v.-visible spectra of (A): (a) **(1a)**, (b) **(1b)**, and (c) **(3)**; (B): (d) Zn-**(1a)**, (e) Zn-**(1b)**, and (f) Zn-**(3)**, in  $\text{CHCl}_3$  at 21 °C.

The two isomers **(1a)** and **(1b)** cannot be interconverted over 5 h in boiling toluene.

The Zn derivatives Zn-**(1a)**,<sup>†</sup> Zn-**(1b)**<sup>†</sup> and Zn-**(3)**<sup>†</sup> [ $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , 2.2 equiv. for **(1)**, and 1.1 equiv. for **(3)**,  $\text{CHCl}_3$ ] and the Cu derivative Cu-**(1a)**<sup>†</sup> [ $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , 2.2 equiv.,  $\text{CHCl}_3$ ] were prepared in quantitative yield under mild conditions without heating in an ultrasonic bath within 10 min.: FAB mass spectra Zn-**(1a)**:  $M^+ + \text{H}$ , 2409.62; Zn-**(1b)**:  $M^+ + \text{H}$ , 2409.63; for  $\text{Zn}_2\text{C}_{144}\text{H}_{89}\text{N}_{24}\text{O}_8$  calc. 2409.59; Cu-**(1a)**:  $M^+ + \text{H}$ , 2407.61; for  $\text{Cu}_2\text{C}_{144}\text{H}_{89}\text{N}_{24}\text{O}_8$  calc. 2407.58.

The u.v. absorption spectra of the new compounds **(1a)**, **(1b)**, **(3)**, Zn-**(1a)**, Zn-**(1b)**, Zn-**(3)**, and Cu-**(1a)**, besides the typical bands of the porphyrin chromophore, show a broadened band in the azobenzene  $\pi \rightarrow \pi^*$  region between 320 and 380 nm.

The u.v.-visible spectral data for the three species and their Zn and Cu derivatives are collected in Table 1; compared to the tetraester **(3)**, the Soret bands of the two porphyrin dimers **(1a)** and **(1b)** are only insignificantly blue-shifted (3 and 1 nm). In the long wavelength region the three spectra are very similar.

These results are consistent with the long distance between the two porphyrin systems in **(1)**, so that there are only weak interactions. The red-shift of the azobenzene band to 344 nm in **(1a)** and 342 nm in **(1b)** is remarkable compared to the porphyrin tetraester **(3)** showing the azobenzene maximum at 330 nm. This indicates exciton coupling between the azo-groups and the porphyrins, or charge transfer interactions between the closely arranged azobenzene units in the pentacyclic compounds.

**Table 1.** U.v.-visible data (in  $\text{CHCl}_3$ ).

Compound	$\lambda_{\text{max}}/\text{nm}$
<b>(3)</b>	330, 425, 517, 551, 591, 648
Zn- <b>(3)</b>	330, 430, 518, 558, 596
<b>(1a)</b>	344, 422, 518, 552, 590, 646
Zn- <b>(1a)</b>	342, 426, 518, 577, 594
Cu- <b>(1a)</b>	342, 417, 500, 540, 574
<b>(1b)</b>	342, 424, 518, 552, 592, 650
Zn- <b>(1b)</b>	339, 426, 519, 558, 598

The absorption bands of the *E*-azobenzene units of **(1a)** and **(1b)** in the 340 nm u.v. region are of equal intensity. Furthermore the  $^1\text{H}$  n.m.r. spectrum of **(1a)** can be definitely assigned to a double layered porphyrin structure with all azobenzene units in the *E*-geometry. These facts prove that all azobenzene groups are *E* in both isomers and by this the existence of structural isomers is assigned to the restricted rotation of the amide groups and the different spatial arrangement of the azobenzene links.

4,4'-Azobenzene dicarbamide derivatives change their configuration<sup>13</sup> from *E* to *Z* under irradiation with u.v. light. Similarly the *E/Z* isomerization of the four azo groups in **(1a)** should be possible and give interesting spectroscopic effects because the distance between the two porphyrin systems becomes shorter in the *Z* form, as CPK models show. To get information about this, photochemical investigations are in progress.

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