

Figure 2. Arrangement of the molecules a) in the unsolvated yellow crystal (short $S \cdots N \equiv C$ contacts of 3.30, 3.32, and 3.36 Å are indicated by dotted lines) and b) in the violet PhCN-solvated crystal (two crystallographically independent PhCN molecules are included in the spatial cavity; short $S \cdots N \equiv C$ contacts $(S \cdots N = 3.01 \text{ Å})$ are observed along the *c* axis not shown in this view).

(4.165), 433 (sh, 4.096), 515 (sh, 4.470), 544 nm (4.513) in CH_2Cl_2 at 25 °C] closely resembles that of **2B** · CH_2Cl_2 crystal [KBr disk; λ_{max} (relative intensity) = 326 (1.00), 407 (0.28), 568 (sh, 0.84), 607 nm (0.87)]. Although the precise proportion of 2A and 2B in solution is not known, the cyclic voltammogram of 2 can be explained by assuming the presence of only one conformer (2B). Thus, four reversible, one-electron reduction waves were observed at +0.28, +0.06, -0.95, and -1.10 V vs the saturated calomel electrode $(0.1 \text{ M } n\text{Bu}_4\text{NBF}_4 \text{ in CH}_2\text{Cl}_2, \text{Pt}$ electrode, scan rate 100 mVs⁻¹, 25 °C). The electron affinity of **2** is similar to that of TCNQ ($E_1^{\text{red}} = +0.30$ V) and much higher than those of 1 or its bis(dicyanomethylene) derivative^[13] $(E_{p}^{red} = -1.16 \text{ and } -0.77 \text{ V}, \text{ respectively, under the same condi$ tions). Thus, by the reaction with iodide 2 was readily reduced to the radical anion, which could be isolated as stable salts.^[14] Furthermore, 2 gave charge transfer complexes with some donors despite its severely deformed geometry. The moderate electrical conductivity ($\sigma = 3.4 \times 10^{-2} \text{ S cm}^{-1}$) of the 1:1:1 complex of 2, tetrathiatetracene, and H_2O is noteworthy.

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A Calix[4]arenoporphyrin**

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Due to the potential biological or other catalytic activity of supramolecular arrays,^[1, 2] much interest has been focused on the synthesis and chemistry of such assemblies. Recently, large cyclic structures were obtained based on porphyrin subunits as building blocks.^[3] It was shown that supramolecular arrays of porphyrins with higher order structures act not only as unique molecular recognition species but also as enzyme-mimicking catalytic sites.^[4]

Among the different building blocks that were studied for the synthesis of artificial receptor molecules, calixarenes,^[5] cyclodextrins, and resorcinol-based cavitands are particularly useful.^[6] Recently, considerable interest has been given to the use of calixarenes as platforms for the construction of supramolecular receptor assemblies.^[7] Calixarenes are readily accessible cyclic polyphenols which are chemically transformable in a selective fashion, so that they are used as building blocks for larger

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and more sophisticated molecular assemblies. Calixarenes have been very actively investigated, and a great number of derivatives of different types have been synthesized which display a variety of substrate binding and reactivity features.^[8]

Aiming at the synthesis and elaboration of large systems based on both calixarene and porphyrin units, we utilized calixarenes as molecular platforms that allow the synthesis of supramolecular porphyrin assemblies with well-defined, conformationally fixed superstructures. Complexation of calix[4]arenes, which possess strong ion-bonding properties, with porphyrins, which are pH-dependent photoactive chromophores, can potentially lead to new molecular receptors for the development of efficient sensing agents. Several porphyrin–calixarene complexes have been synthesized; however, the yields were usually less than one percent, or the complex contained only one porphyrin subunit.^[9]

We adopted the Zinke–Cornforth procedure,^[5b, 10] with some minor modifications, for synthesizing a calix[4]porphyrin. Two main issues addressed in the planning of our synthesis were solubility and steric congestion due to the large size of the porphyrin chromophore. By careful design and molecular modeling, we determined that a porphyrin with unsubstituted peripheral positions on its upper half would minimize any steric congestion among adjacent porphyrins, but that the resulting calixarene would probably have the $\alpha,\beta,\alpha,\beta$ -atropisomeric conformation. On the lower half, ethyl groups were placed at the peripheral pyrrole subunit carbon atoms to increase solubility of the final product.

The upper half of the porphyrin was prepared by condensation of *p*-anisaldehyde and pyrrole in trifluoroacetic acid (TFA), resulting in methoxyphenyldipyrromethane (1) in 51% yield (Scheme 1).^[11] Vilsmeier bisformylation of 1 gave 2 (86% yield), which reacted with 2,3,7,8-tetraethyldipyrromethane (3) to afford 4-(12,13,17,18-tetraethylporphyrinyl)anisole (4) in 49% yield. The methoxy group was then cleaved with BBr_3 to give 4-(12,13,17,18-tetraethylporphyrinyl)phenol (5) in quantitative yield. Nickel was then inserted (in 97% yield) to prevent any adverse interactions of the central nitrogen atoms of the porphyrin in the subsequent reactions. Heating the nickel(II) complex of 5 at reflux in dioxane containing NaOH gave a mixture of the monobenzylalchohol porphyrin 6 (major product, 61 % yield), the starting porphyrin 5-Ni, and the bis-(benzylalcohol)porphyrin 7 (9% yield). Heating the mixture at reflux in diphenyl ether containing NaOH followed by a workup with ethyl acetate gave a precipitate, which was dissolved in DMF and subjected to chromotography on Sephadex G-25-300. The fastest running band was collected to give calix[4]arenoporphyrin 8 in 60% yield.

¹H NMR spectroscopy of 8 (in $(CD_3)_2SO$) showed broad signals, which were only marginally temperature dependent, at $\delta = 9.85$ (meso-H), 9.11 (β -H), 7.44 (OH), 7.34 (aromatic H), and 3.98 (methylene bridge). Peaks for the ethyl substituents appeared at $\delta = 4.13$ and 1.69. The methylene bridge carbon atoms were at $\delta = 29.8$ in the ¹³C NMR spectrum. Spectrophoto metry showed a broadened Soret band at $\lambda_{max} = 404$ nm (porphyrin monomer 5-Ni: 399 nm). The calix[4]arenoporphyrin 8 was further characterized by mass spectrometry, elemental analysis, and X-ray diffraction studies. Figure 1 shows the molecular structure of 8.^[12] Surprisingly, the molecule adopts the cone $(\alpha, \alpha, \alpha, \alpha)$ conformation. Of the four configurations possible for the calix[4] arenoporphyrin (Figure 2), we anticipated, based on molecular modeling and other energetic considerations, that the molecule would adopt the $\alpha, \beta, \alpha, \beta$ configuration; we also expected that π - π stacking of the type shown in Figure 2 would be reasponsible for the broadening in the ¹H NMR spectrum. Fig-



Scheme 1. Synthesis of calix[4]arenoporphyrin 8.

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Figure 1. Molecular structure of calix[4]arenoporphyrin 8; A: side view, B: top view. Hydrogen atoms have been omitted for clarity.



Figure 2. Schematic representation of the four major atropisomeric conformations of 8, and the anticipated aggregation complex for the $\alpha, \beta, \alpha, \beta$ conformer (see text).



Figure 3. Molecular structure of the aggregated dimer of 8; A: side view, B: top view. Hydrogen atoms have been omitted for clarity.

ure 3 shows the interactions which exist between two neighboring molecules of calix[4]arenoporphyrin, and fully explains the existence of the $\alpha, \alpha, \alpha, \alpha$ conformation. Aggregation between two molecules to give a cogwheel arrangement is clearly a dominating phenomenon, and this leads to a self-assembling supramolecular array which, as the nickel(II) complex, we have thus far been unable to uncog.

The unit cell in the crystal structure of 8 has the dimensions a = b = 23.51, c = 100.61 Å and a volume of 55609 Å³. A large void exists in which methanol molecules of solvation partially occupy twelve sites; two more methanol sites exist within the cavity of each calix[4]arenoporphyrin. Inclination angles of the phenyl groups (with respect to the best plane of methylene groups) for the calixporphyrin complex are 130.1. 123.9, 118.5, and 126.2°; calix[4](p-tert-butylbenzene) has an inclination angle of 123°. [5b] Deviations from this value are usually caused by packing effects, or in this case, aggregation of the calix[4]arenoporphyrin units. Another indicator of the strain placed on the calixarene by the porphyrin subunits are the larger O-Odistances of 2.513, 2.872, 2.790, 2.479 Å; the average value in calix[4](*p-tert*-butylbenzene) is 2.650 Å.^[5b] The asymmetric unit consists of two calix molecules, each of which forms an aggregate with its centrosymmetrically related pair. A fourfold screw axis along the c axis generates the packing system. Whereas one molecule occupies the space at the center of the cell, the other is positioned at the corners; this forms channels in the lattice packing model.

The structural features of 8 are unique. We consider the dimeric cogwheel compound derived from 8 to be a remarkable example of a robust, definitively structured, self-assembled supramolecular array of versatile chromophores. Further studies focus on the syntheses of calix[6]- and calix[8]arenoporphyrins, and formation of free base as well as other metal complexes. Based on the fact that the calix[8]arenoporphyrin might

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afford a cyclic cogged dimer with sixteen π -stacked tetrapyrrole units, further studies are aimed at developing molecules which are potential models for systems such as the array of tetrapyrroles in the light-harvesting component of the bacterial light harvesting complex LH2.^[14] Indeed, we note that the B800 and B850 components of the light-harvesting complex II in *Rhorospirillum molischianum* consist of eight and sixteen units of bacteriochlorophyll, respectively.^[15]

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- [12] Crystallographic details for 8: $C_{141.75}H_{128}N_{16}Ni_4O_{5.75}$, dark green, octahedral crystal (0.15 × 0.10 × 0.10 mm), tetragonal space group P4,22 (no. 92); a = b = 23.510(3), c = 100.61(2) Å, V = 55609(16) Å³, Z = 16. Of 33061 reflections measured, 15009 were unique and 9740 observed ($R_{int} = 0.033$, $T_{\rm min} = 0.90, T_{\rm max} = 0.85, \mu = 1.047 \, {\rm mm^{-1}}, \rho_{\rm calcd} = 1.138 \, {\rm g\,cm^{-3}}); R1 = 0.1142$ (observed data, $I > 2\sigma(I)$) and wR2 = 0.3483 (all data) for 2571 parameters. Data were collected at 113(2) K on a Siemens Hi Star multiwire proportional counter diffractometer mounted on a Rigaku RU300 rotating anode equipped with a 3.0×0.3 mm focal cup and Göbel mirrors (Cu_{Kx} irradiation; $\lambda = 1.54178$ Å, ω scan mode, $2\theta_{max} = 90.2^{\circ}$). The structure was solved by direct methods and refined (based on F^2 with all independent data) by full-matrix least-squares methods (Siemens SHELXTL Version 5.03). A total of fourteen methanol sites were found; twelve were located in regions of void, and the other two in the calixarene cavities. All sites showed only partial occupancy summing to a total of 1.75 methanol molecules. With the exception of the solvent molecules, non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated by idealized geometry and treated as riding using isotropic thermal parameters (but not on the solvent molecules). The data were corrected for absorption [13]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publica-

tion no. CCDC-100 523. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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Synthesis, Structure, and Double Olefin Extrusion of All Three Diastereomers of 2,2,6,6-Tetrakis(4-chlorophenyl)-3,7-dimethyl-4phenyl-1,5-dioxa- $4\lambda^5$ -phosphaspiro[3.3]heptane**

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In the course of our study on heterocyclobutanes $1^{(1)}$ bearing highly coordinated main group elements at the position adjacent to the heteroatom we have reported the syntheses and isolation of intermediates of the Wittig and Peterson-type reactions.^[2] Recently we also achieved the synthesis of tetracoordinate and pentacoordinate 1,2-oxathietanes and their thermolysis to the oxirane with retention of configuration.^[3] Our studies on the influence of ring size on the stability of 1,2-oxaphosphetanes led to the synthesis of **2**, the first stable pentacoordinate spirophosphorane with two 1,2-oxaphosphetane rings; the stability is attributed to the trifluoromethyl groups at the 4-position.^[4, 5]



Unexpectedly, however, double olefin extrusion from 2 was unsuccessful, because of the electronic effect of the strong electron-withdrawing groups. Taking into consideration the bonding character of equatorial bonds in a trigonal-bipyramid (TBP) structure, an electron-releasing group such as an alkyl group at the 3-position is expected to stabilize a TBP structure sufficiently even in the absence of a strong electron-withdrawing group. The introduction of such a substituent at the 3-position may also lead to kinetic stabilization toward hydrolysis by steric protection, as observed in the tetracoordinate 1,2-oxathietanes.^[3a] We now report the synthesis, crystal structures, and thermolysis of all three diastereomers of 2,2,6,6-tetrakis(4chlorophenyl)-3,7-dimethyl derivatives **3**.

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