ated cyclooctatriene acts as a slow donor of tritium resulting in the formation of $C_8H_7T^{\bullet-}$, Scheme I. This mechanism is supported by the fact that addition of independently synthesized dideuteriocyclooctatriene to a $C_8H_8^{\bullet-}$ solution results in formation of $C_8H_7D^{\bullet-}$.

Acknowledgment. We wish to thank the National Science Foundation (Grant CHE-9011801) for support of this work. We also thank Dr. Richard Reiter for simulating the EPR spectra.

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Synthesis and Characterization of the First Water-Soluble Closely Interspaced Cofacial Porphyrin Dimer

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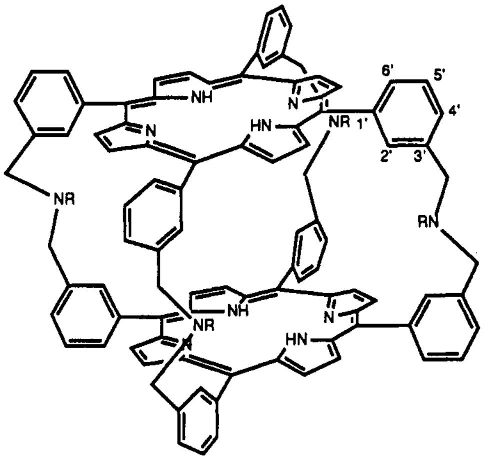
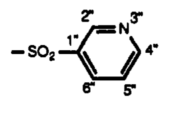
Received February 6, 1991

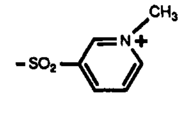
Summary: The first closely spaced quadruply bridged water-soluble cofacial dimer (5) was successfully synthesized by the reaction of porphyrin 2 with sulfonamide 3 followed by N-methylation with methyl iodide. The conformations of 5 and its precursor 4 are largely dependent on the solvent, and the solvent effect is inhibited by protonation or metalation of the porphyrin cores.

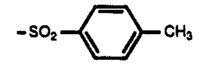
Metal-centered cofacial dimeric prophyrins have been recognized as intriguing compounds since they were first prepared and reported.[1] They have been offered as putative models for the study of cytochrome c_3,[2] cytochrome-c-oxidase,[3] and other[4,5] metallo enzymes. Binding affinities of dioxygen and carbon monoxide[6] by metal-centered cofacial dimeric prophyrins have been studied, and it has been shown that they may serve as effective catalysts for the four-electron reduction of dioxygen to water.[3] These agents have been employed in the study of antiferromagnetic coupling as seen with superoxide dismutase and cytochrome-c-oxidase.[7] To this date, studies have been restricted to organic solvents. Cofacial dimeric tetraphenylporphyrins may be singly, doubly, triply, or quadruply bridged. The number of bridges determine the rigidity of the structure, and the length of the bridges determine the closeness of interspacing of the porphyrin planes.

With the exception of the single compound prepared by Kagan in 1977,[8] quadruply bridged *closely interspaced* dimeric tetraphenylporphyrins were unknown. We report now the synthesis of and preliminary observations on the first *closely spaced* water-soluble cofacial dimeric tetraphenylporphyrin 5 and its biszinc(II) complex (Zn_2–5).



4 R =


, 5 R =


6 R =


The synthesis of 5 is based on recently devised technology for the synthesis of quadruply two- and three-atom, aza-bridged cofacial tetraphenylporphyrins.[9] Porphyrin

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Table I. UV/Vis Spectra of Dimers and Monomers in DMSO and $CHCl_3$

compd	solvent	soret band width at half peak height (nm)	UV/vis λ_{max} (nm) ($\epsilon \times 10^{-3}$ cm^{-1} M^{-1})
2	$CHCl_3$	12	419 (324), 515 (16.1), 549 (7.2), 589 (5.5), 646 (3.4)
2	DMSO	12	419 (315), 516 (15.9), 549 (7.2), 590 (5.5), 646 (3.4)
4	$CHCl_3$	19	414[a] (415), 514 (23.6), 550 (11.2), 591 (7.1), 647 (3.7)
4	DMSO	21	407 (463), 518 (15.8), 561 (9.6), 598 (4.4), 658 (3.0)
6	$CHCl_3$	19	414[b] (447), 515 (22.3), 550 (9.3), 591 (7.5), 647 (5.7)
6	DMSO	20	407 (520), 520 (18.1), 558 (9.9), 597 (4.7), 655 (3.8)

[a] The soret bands have shoulders at 406 (314). [b] The soret bands have shoulders at 407 (350).

5 incorporates the following structural features: (1) substitution on the porphyrin meso-positions to prevent oxidation of the porphyrin rings; (2) solubility in aqueous solutions; (3) cationic charged groups to attract anionic species into a cavity for interaction with the metal moieties of the porphyrin rings; and (4) a relatively small internal cavity.

α-Bromo-*m*-tolualdehyde (**1**) was prepared by a literature procedure[9,10] with benzene as the solvent. Condensation of **1** with pyrrole in chloroform, following the procedure of Lindsey[11] and separation by chromatography on silica gel using chloroform/methanol as an eluent, provided *m*-(bromomethyl)tetraphenylporphyrin (**2**)[9] in 24% yield. Reaction of *m*-pyridinesulfonic acid with phosphorus pentachloride (120 °C, for 12 h in $POCl_3$) followed by treatment with an excess ammonium hydroxide solution provided *m*-pyridinesulfonamide **3** (two steps, 68% yield).[12] High dilution coupling (10^{-3} M) of porphyrin **2** and sulfonamide **3** in the presence of excess Cs_2CO_3 (rt, for 16 h in DMF) and purification by chromatography on silica gel using chloroform/methanol as an eluent afforded the cofacial quadruply bridged porphyrin dimer **4** in 12% yield. Proof of structure **4** was obtained by FABMS, ^1H and ^{13}C NMR, and UV/vis spectral techniques.[13] The UV/vis and NMR spectroscopic properties display characteristics quite different from monomeric porphyrins such as **2**. The ^1H NMR spectrum shows distinctive shielding effects on the pyrrolic NH protons ($\Delta\delta = -1.5$) and the β-pyrrolic protons ($\Delta\delta = -0.7$). UV/vis spectroscopy shows a broadened, blue-shifted soret band compared with **2** (see Table I). These spectral characteristics indicate that the two prophyrin rings are parallel and in close proximity such that a π-π interaction exists between them.[14] The biszinc complex of **4** (Zn_2-**4**) was prepared in quantitative yield by reaction of **4** with excess $Zn(OAc)_2$ (rt, 5 h in chloroform/methanol): FABMS 2084 (calculated for $C_{116}H_{80}N_{16}O_8S_4Zn_2$ [M^+] *m/z* 2084); UV/vis (DMSO) 413 (sh, 160), 422 (377), 560 (17.0), 600 (5.2).

The target tetracationic porphyrin dimer **5** was prepared in 70% yield by the action of excess methyl iodide in chloroform/acetone solution of **4** (65 °C, for 12 h) followed by separation on a reverse-phase plate (Whatman, PLKC18F) using acetone/water/NaCl as an eluent. The chloride salt was obtained by ion exchange with resin in the chloride form (Dowex 1X8-100/Cl^-). **5** is readily soluble in DMF, DMSO, and aqueous solutions containing less than 0.5% DMF or DMSO and slightly soluble in water, methanol, and acetone. The FABMS spectrum shows the molecular peak [M^+] *m/z* 2016 (calculated for $C_{120}H_{96}N_{16}O_8S_4$ [M^+] *m/z* 2016), and $M^+ - CH_3$ fragment (2001): UV/vis (DMSO) 409 (351), 519 (17.4), 556 (13.1), 598 (9.3), 658 (7.6); emission (DMSO) max, nm (rel intens) 660.5 (11.22), 723.4 (1.0).

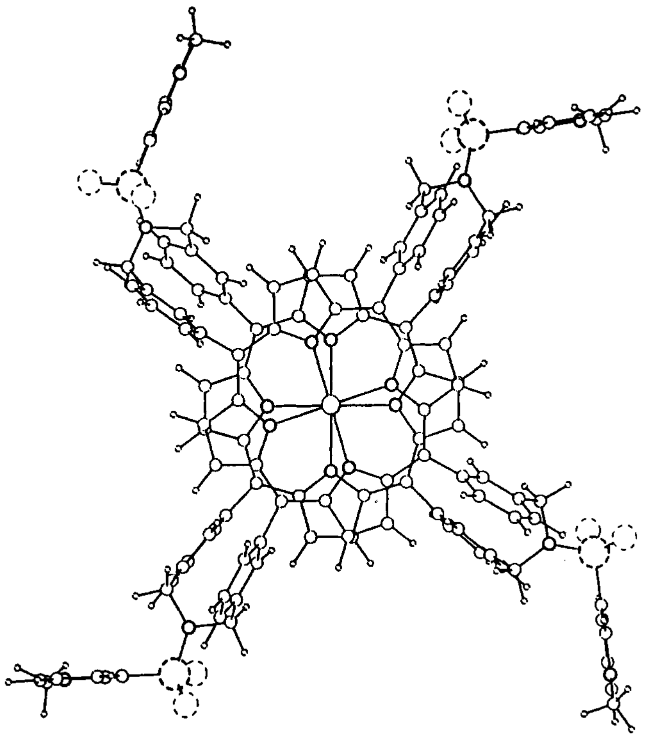

Figure 1. Top views of the minimized structure of Zn_2-**5** showing the symmetrical conformation with the *N*-methylpyridine moiety pointing outside the cavity. For details of the calculations see ref 16.

The biszinc complex of **5** (Zn_2-**5**) was prepared in quantitative yield by reaction of excess $Zn(OAc)_2$ with **5** in DMF solution (95 °C for 2 h). The FABMS spectrum shows a base peak at 2129 corresponding to $M^+ - CH_3$ (calculated for $C_{120}H_{92}N_{16}O_8S_4Zn_2$ [$M^+ - CH_3$] *m/z* 2129). UV/vis spectroscopy shows a similar spectrum to that of Zn_2-**4** (see table). ^1H NMR spectrum of Zn_2-**5** supported the proposed structure, and all resonances were assignable and proportioned.[15]

Molecular dynamics calculations in the gas phase for **4** and **5** indicate that both have symmetrical conformations with the pyridine and *N*-methylpyridine moieties pointing

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(13) ^1H NMR ($CDCl_3$) δ −4.34 (s, 4, NH), 4.66 (s, 16, CH_2), 7.04 (s, 8, H-2′), 7.52 (t, *J* = 6.5 Hz, 4, H-5″), 7.58 (t, *J* = 7 Hz, 8, H-5′) 7.72 (d, *J* = 7 Hz, 8, H-4′), 7.94 (d, *J* = 7 Hz, 8, H-6′), 8.14 (s, 16, β-pyrrolic H), 8.25 (d, *J* = 7 Hz, 4, H-6″), 8.76 (d, *J* = 7 Hz, 4, H-4″), 9.11 (s, 4, H-2″); ^{13}C NMR ($CDCl_3$) 49.5 (CH_2), 118.4 (meso-C), 123.7, 127.4, 128.6, 132.6, 133.2, 134.9, 135.1, 138.0, 142.0, 148.2, 153.1, 153.4, 153.7; FABMS 1956 (calcd for $C_{116}H_{84}N_{16}O_8S_4$ [M^+] *m/z* 1956); Emission ($CHCl_3$) max, nm (rel intens) 651.7 (8.07), 717.8 (1.0).

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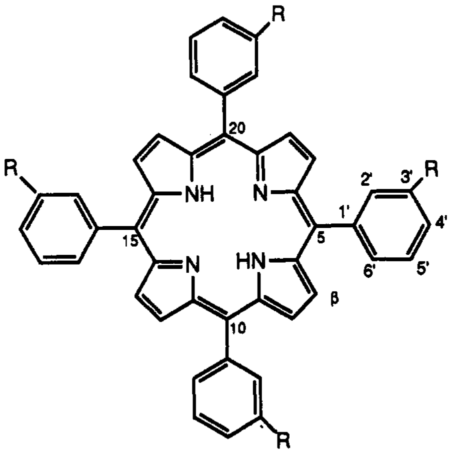
(15) ^1H NMR (acetone-d_6) 4.94 (br s, 28, CH_2 and N-CH_3), 7.35 (s, 8, H-2′), 7.78 (t, *J* = 7 Hz, 8, H-5′), 7.88 (d, *J* = 7 Hz, 8, H-4′), 8.10 (d, *J* = 7 Hz, 8, H-6′), 8.21 (s, 16, β-pyrrolic H), 8.73 (t, *J* = 7 Hz, 4, H-5″), 9.39 (d, *J* = 7 Hz, 4, H-6″), 9.55 (d, *J* = 7 Hz, 4, H-4″), 9.95 (s, 4, H-2″). In DMSO-d_6, the peak at 4.94 appears as two singlets: δ 4.82 (s, 16, CH_2), 4.95 (s, 12, N-CH_3); FABMS 2129 (calculated for $C_{120}H_{92}N_{16}O_8S_4Zn_2$ [$M^+ - CH_3$] *m/z* 2129); UV/vis (DMSO) 413 (sh, 185), 421 (347), 559 (17.6), 598 (4.2).

outside the cavity (Figure 1).[16] This suggests that, in the absence of strong interactions between the solvent and the solute, these porphyrins in solution will exist in a symmetrical conformation and their ^{1}H NMR will be assignable as shown for 4 in the data of ref 13. Since **5** is not soluble in $CDCl_3$, its ^{1}H NMR spectrum was taken in DMSO-d_6 and acetone-d_6. The ^{1}H NMR in DMSO-d_6 shows four NH signals in the region from δ −5.2 to −6.1, two benzylic proton signals, and two methylic proton signals in the region δ 4.8–5.7 and a complex aromatic region from δ 7.0 to 10.0.[17] In contrast, the ^{1}H NMR spectra of the corresponding tetraprotonated species (prepared by adding excess trifluoroacetic acid to **5**) in different solvents (acetone-d_6, DMSO-d_6, CD_3OD, and CF_3COOD) show assignable peaks. For example, the ^{1}H NMR in acetone-d_6 shows a pyrrolic NH proton at δ −4.3, a broad signal at δ 5.0 corresponding to the benzylic and methylic protons and integrating 28 protons, four phenylic proton signals at δ 7.1, 7.9, 8.0, and 8.2 each integrating 8 protons, one meso signal at δ 8.25 integrating 16 protons, and four pyridinic proton signals at δ 8.75, 9.4, 9.7, and 10.1 each integrating 4 protons. These results are anticipated from the structure of tetraprotonated **5**.

Comparison of the ^{1}H NMR spectrum of **5** to that of its biszinc and tetraprotonated derivatives in DMSO shows a dramatic conformational switch between them. This indicates that DMSO interacts with the porphyrin moieties and this interaction is inhibited by inducing species such as Zn^{2+} or H^+ in the center of the porphyrin rings. The same phenomenon was observed with other dimeric porphyrins such as **4** and **6**. The conformational change on transfer from $CDCl_3$ to DMSO-d_6 with these dimeric porphyrins can also be observed from their UV/vis spectra by the blue-shifting of the Soret band and red-shifting of visible bands (see table). The emission spectrum of the dimeric porphyrin **4** in DMSO is red-shifted and its intensity is increased by 30% compared to that in $CHCl_3$, whereas the emission spectrum of the monomeric porphyrin **7** in DMSO is unchanged and its intensity is 90% higher than that in $CHCl_3$. The increase in the intensity of the emission band by DMSO is due to general solvent effects which are dependent on the dielectric constant of the solvent.[18] The relatively low effect of DMSO on the intensity of the emission bands in the dimer may be attributed to a specific interaction between DMSO and the fluorophore molecules of the dimer. Monomeric porphyrins such as **2** and **7** do not show any ^{1}H NMR or UV/vis spectral changes upon switching from $CDCl_3$ to DMSO-d_6. Varying the concentration of all the dimeric porphyrins examined from 1×10^{-2} to 5×10^{-6} M caused no change in the UV/vis and ^{1}H NMR spectra. The combined results reveal that the source of the effect seen in DMSO solutions is a result of an interaction between DMSO and the two porphyrin rings in the dimer, rather than aggregation,[19] and this interaction causes the two porphyrin rings to approach closer to each other as judged by the upfield shift of the pyrrolic N-H resonance and the quenching of the emission band intensity. Further work is currently underway to explore this phenomenon and to prepare other metal complexes of **5** for studies in aqueous and organic solutions.



2 R = CH_2Br
7 R = CN

Acknowledgment. This work was supported from grants from PROTOS corporation and the National Institutes of Health.

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[16] The starting geometries of structures 4, 5, and Zn_2–5 were generated in the 2D molecular construction routine of Quanta (Polygen, Corp.) using the X-ray file of tetraphenylporphyrin (TPP) and minimized structures of pyridinesulfonamide and its *N*-methyl derivative and they were extensively minimized in $CHARM_m$ with steepest descents and adopted basis Newton-Raphson.

[17] Similar spectrum was obtained using acetone-d_6 as a solvent.

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[19] The same phenomenon was observed in acetone.

Synthesis and Conformational Behavior of Fenestrindans (Tetrabenzo[5.5.5.5]fenestranes) with Four Bridgehead Substituents[1]

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Received February 26, 1991

Summary: all-cis-Tetrabenzo[5.5.5.5]fenestranes (fenestrindans) with four bridgehead substituents (**4**-**10**) and two doubly bridged, centrohexacyclic analogues, the bis-*endo*-peroxide **11** and the bis-disulfide **12**, have been synthesized from the tetrabromofenestrindan **3**. Pronounced steric interactions between the substituents at opposite bridgehead positions have been revealed by NMR and DNMR spectrometry, showing remarkable size-dependent hindrance of the degenerate interconversion of the two S_4 symmetric conformers of the fenestrindans.

Fenestranes have attracted much interest because of the geometric constraints induced by the mutual fusion of the

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[1] (a) Benzoannelated Centropolyquinanes, Part IX. Presented in part at the Sixth European Symposium on Organic Chemistry (ESOC VI), Belgrade, Yugoslavia, 1989, paper B-O 017. Part VIII: Paisdor, B.; Kuck, D. *J. Org. Chem.*, in press. (b) For a review on centropolyindans, see: Kuck, D. In *Quasicrystals, Networks, and Molecules of Fivefold Symmetry*; Hargittai, I., Ed.; VCH Publishers: New York, 1990; Chapter 19.

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