J. Am. Chem. Soc. **1983**, *105*, 6747–6749

We are currently seeking further explanation of the dependence of $\Delta\delta/\Delta T$ upon anomeric configuration by measuring temperature dependences in additional compounds and solvents and by measuring hydrogen–deuterium exchange rates. The dependence of $\Delta\delta/\Delta T$ upon anomeric configuration and also its possible ramifications for other NMR conformational parameters such as rates of exchange with solvent protons[10b,16] should be taken into consideration in future carbohydrate conformational analyses that employ these parameters. Such applications may become increasingly frequent as the recent advances in the identification and availability of biologically important carbohydrates continue.

Acknowledgment. We thank Mr. Robert Thrift of the Gray Freshwater Biology Institute (Navarre, MN) for his assistance and also that institute for its generosity in making their spectrometer available to us. We also thank Dr. Richard Ramette of Carleton College, the author of the least-squares and plotting program. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. This research was also supported by a Northwest Area Foundation Grant of Research Corporation.

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Enforced Deformation of Porphyrins by Short-Strap Bridging

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X-ray crystallographic studies on porphyrins[1,2] have long shown that slight deviations from coplanarity of the macrocyclic core may occur, usually as a "ruffling" of essentially planar pyrrolic subunits. It is often assumed that such distortions derive principally from crystal packing forces. This phenomenon is best exemplified by the two dimorphs of nickel octaethylporphyrin where in one modification[3] all four pyrrolic rings are coplanar while in the other[4] the pyrrolic rings are alternately tilted by ~14° with respect to the median plane. We wished to examine more highly deformed porphyrin derivatives, to ascertain whether such deformations might be of importance in their chemistry (as, for example, the relation of doming to hemoglobin cooperatively[5]), and to establish the limits beyond which deformation results in a loss of stability or aromaticity of the system. system.

A logical approach to a permanently deformed porphyrin suggests a covalent clasp or bridge be applied to diametrically opposed β-positions. As a porphyrin is unlikely to bend to accommodate the *formation* of such a strap, we chose to construct a porphyrin system with the strap already in place following a strategy that we have previously employed for the preparation of covalently linked dimeric porphyrins.[6] For reasons of stability we chose to employ a chain consisting solely of methylene units. The syntheses proceeded as outlined in the scheme[7] to give the strapped bis(dipyrromethanes) **14**, which were then cyclized under high-dilution conditions in the presence of toluenesulfonic acid. This intramolecular coupling proceeds through a porphodimethene intermediate, **15**, in which opposite meso positions are sp^3 hybridized. This allows for a folded tent-like geometry that can

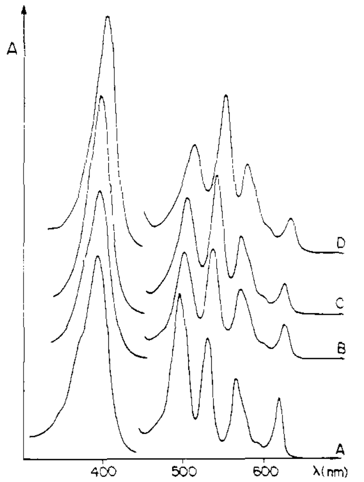
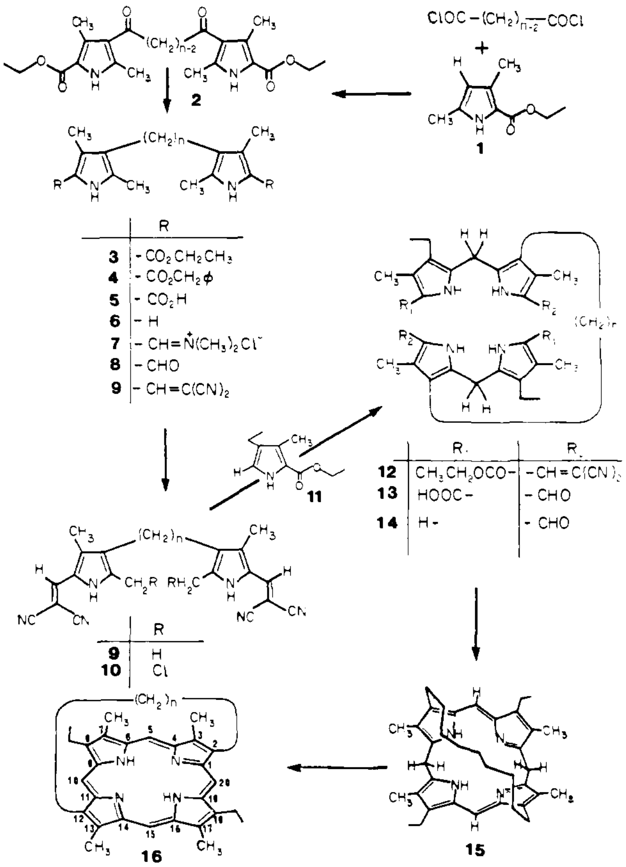


Figure 1. Optical spectra (CH_2Cl_2) of (A) etioporphyrin II, (B) **16**, *n* = 11, (C) **16**, *n* = 10, and (D) **16**, *n* = 9.

Scheme I



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(7) Satisfactory elemental analyses and NMR spectra (^1H and ^{13}C) were obtained for all new compounds.

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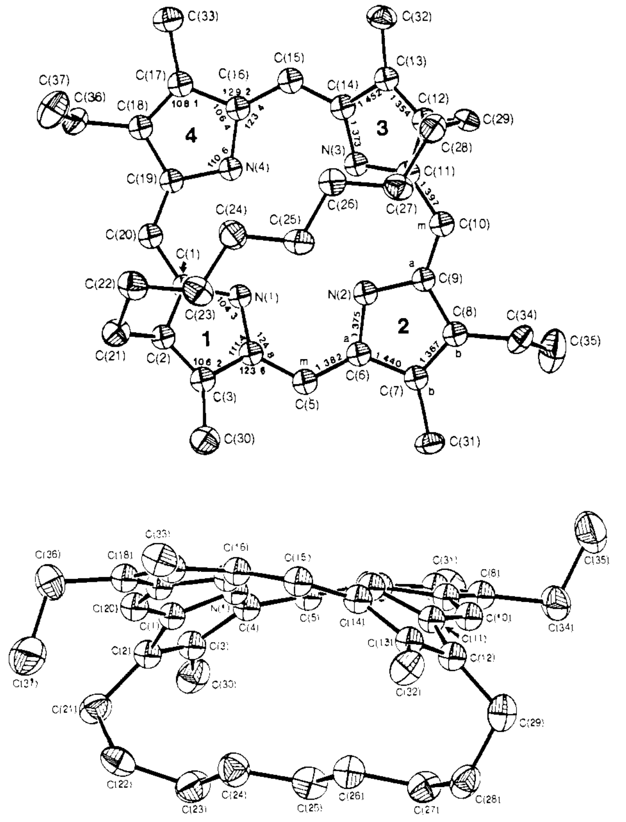

Figure 2. ORTEP drawings of **16**, $n = 9$. Bond distances and angles have errors less than 0.005 Å and less than 0.4°, respectively.

accommodate a shorter bridging chain at the macrocycle-forming stage than a preformed porphyrin could. Oxidation of the porphodimethane **15** to the porphyrin **16** will then flatten the macrocycle simultaneously "drawing the bowstring" to the extent the bridge permits.

The first porphyrin prepared in this manner **16**, $n = 11$, was obtained in a 40% yield from **14**. However, its optical spectrum (Figure 1) was almost identical with that of etioporphyrin II (where the strap is replaced by ethyl groups at positions 2 and 12), suggesting that at a length of 11 the methylene strap introduces essentially no distortion! Such is not the case as the chain is progressively shortened. With a 10-carbon chain (**16**, $n = 10$) the optical spectrum showed a small though significant change (Figure 1), and this change is even more pronounced with the shortest chain (Figure 1) that we have been able to incorporate. Here the nine-carbon chain generates a porphyrin (**16**, $n = 9$) that is severely distorted (vide infra). Others have reported the preparation of strapped porphyrins,[8-15] and the crystal structures of an anthracene and pyridine strapped porphyrins have been reported.[16] However, the bimolecular condensations used do not allow for the preparation of strained systems and give, at best, straps equivalent to at least 13 carbon units.

The results of an X-ray structural determination[17] are shown in Figure 2. The angles between the mean planes of rings 1 and 3 and 2 and 4 are 111.5° and 13.5°, respectively. Despite the large change in planarity, examination of the atom pyramidalization and twist angles[18] of the inner porphyrin core indicates that the strain imposed by the strap is distributed fairly evenly throughout the molecule. In view of these observations one might expect a small but nonetheless significant change in aromaticity. Indeed, the appearance of the electronic and NMR spectra for **16**, $n = 9$, is consistent with this observation.

The NH protons are bonded exclusively to N(2) and N(4), suggesting that the canonical form excluding the C_b–C_b double bonds in rings 1 and 3 is favored over the form that includes these double bonds in the aromatic system. In line with this the C_a–C_b bonds of rings 1 and 3 (imino) are longer (0.012 (7) Å), and the C_b–C_b bonds are shorter (0.013 (7) Å) than the corresponding bonds in rings 2 and 4 (amino). While these difference are consistent with our proposal, they are, of course, too small to prove the point crystallographically. Bond distances within each pair of imino and amino pyrrolic rings are comparable to other known undistorted free-base porphyrins.[19-22]

The distortion enforced on the porphyrin **16**, $n = 9$, diminishes the aromaticity only slightly, as measured by the shielding and deshielding by the diamagnetic ring current. Thus the deshielded methine protons resonate at 9.71 and 9.36 ppm compared to 10.12 ppm for etioporphyrin II, while the inner shielded NH protons are observed at −3.06 compared to −3.74 for etioporphyrin II. The bridging nonamethylene chain of **16**, $n = 9$, spans both the shielding and deshielding regions of the diamagnetic ring current. The result is that the porphyrin acts as an internal shift reagent and the methylene protons are observed between −4.5 and 3.5 ppm, with each nonequivalent proton pair being well separated from the others along the entire hydrocarbons chain.

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Registry No. 1, 2199-44-2; **2** ($n = 9$), 87280-98-6; **2** ($n = 10$), 87280-99-7; **2** ($n = 11$), 87281-00-3; **3** ($R = CO_2CH_2CH_3$; $n = 9$), 87280-86-2; **3** ($R = CO_2CH_2CH_3$; $n = 10$), 87280-87-3; **3** ($R = CO_2CH_2CH_3$; $n = 11$), 87280-88-4; **4** ($R = CO_2CH_2Ph$; $n = 9$), 87280-89-5; **4** ($R = CO_2CH_2Ph$; $n = 10$), 87280-90-8; **4** ($R = CO_2CH_2Ph$; $n = 11$), 87280-91-9; **5** ($R = CO_2H$; $n = 9$), 87280-85-1; **5** ($R = CO_2H$; $n = 10$), 87280-84-0; **5** ($R = CO_2H$; $n = 11$), 87280-83-9; **6** ($R = H$; $n = 9$), 87280-92-0; **6** ($R = H$, $n = 10$), 87280-93-1; **6** ($R = H$; $n = 11$), 87280-94-2; **7** ($R = CH = N{=}(CH_3)_2Cl^-$; $n = 9$), 87280-82-8; **7** ($R = CH{=}N^+(CH_3)_2Cl^-$; $n = 10$), 87280-81-7; **7** ($R = CH{=}N^+(CH_3)_2Cl^-$; $n = 11$), 87280-80-6; **8** ($R = CHO$; $n = 9$), 87280-95-3; **8** ($R = CHO$; $n = 10$), 87280-96-4; **8** ($R = CHO$; $n = 11$), 87280-97-5; **9** ($R = H$; $n = 9$), 87280-77-1; **9** ($R = H$; $n = 10$), 87280-78-2; **9** ($R = H$; $n = 11$), 87280-79-3; **10** ($R = Cl$; $n = 9$), 87280-76-0; **10** ($R = Cl$; $n = 10$), 87280-75-9; **10** ($R = Cl$; $n = 11$), 87280-74-8; **11**, 4391-48-4; **12** ($R_1 = CH_3CH_2OCO$, $R_2 = CH{=}C{=}C(CN)_2$; $n = 9$), 87280-71-5; **12** ($R_1 = CH_3CH_2OCO-$, $R_2 = CH{=}C(CN)_2$; $n = 10$), 87280-72-6; **12** ($R_1 =$

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(17) The crystals were monoclinic, space group $P2_1/c$, with $a = 14.774$ (3) Å, $b = 13.823$ (3) Å, $c = 17.634$ (2) Å; $\beta = 103.31$ (1)°, $d_{\text{calcd}} = 1.158$ g cm^{-3} for $Z = 4°$ $C_{37}H_{46}N_4 2CH_3OH$, $M_2 = 610.89$. A suitable crystal (0.40 × 0.40 × 0.40 mm) was sealed in a Lindemann capillary. Data were collected at −100 °C, with a Picker FACS-I automatic four-circle diffractometer [(Mo Kα_1) = 0.70926 Å] with a graphite monochromator and a scintillation counter with pulse-height discrimination. A total of 3723 reflections were measured ($2\theta < 42.0°$), of which 2349 were classed observed [$I > 2.3(I)$]. The structure was solved using MULTAN and was refined by full-matrix least squares. [After location of the porphyrin molecule subsequent difference Fourier synthesis showed the presence of two molecules of methanol of crystallization and a trace of dichloromethane of crystallization (subsequently confirmed by mass spectral data) in a disordered arrangement.] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included but not refined. The final discrepancy index was $R = 0.036$. The final difference map was almost flat (±0.11 (3) e Å^{-3}) except for a few peaks in the solvent region (±0.20 (3) e Å^{-3}).

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CH_3CH_2OCO, $R_2 = CH{=}C(CN)_2$; $n = 11$), 87280-73-7; **13** (R_1 = HOOC, R_2 = CHO; $n = 9$), 87280-68-0; **13** (R_1 = HOOC, R_2 = CHO; $n = 10$), 87280-69-1; **13** (R_1 = HOOC, R_2 = CHO; $n = 11$), 87280-70-4; **14** (R_1 = H, R_2 = CHO; $n = 9$), 87280-65-7; **14** (R_1 = H, R_2 = CHO; $n = 10$), 87280-66-8; **14** (R_1 = H, R_2 = CHO; $n = 11$), 87280-67-9; **15**, 87280-62-4; **16** ($n = 9$)·2MeOH·xClCH$_2$Cl, 87280-59-9; **16** ($n = 9$), 87280-58–8; **16** ($n = 10$), 87280-60-2; **16** ($n = 11$), 87280-61-3; nonanedioyl dichloride, 123-98-8; decanedioyl dichloride, 111-19-3; undecanedioyl dichloride, 45165-01-3; 2,12-diethyl-3,7,13,17-tetramethyl-8,18-(decamethylene)-5,15-dihydroporphyrin, 87280-63-5; 2,12-diethyl-3,7,13,17-tetramethyl-8,18-(undecamethylene)-5,15-dihydroporphyrin, 87280-64-6.

Supplementary Material Available: Table I listing average bond distances, Table II listing the thermal parameters, and Table III listing the final positional parameters are available for compound **16**, $n = 9$ (6 pages). Ordering information is given on any current masthead page.

Uranium–Carbon Multiple Bond Chemistry. 2. Coupling of Bridging and Terminal Carbonyls to an Iron η^1:η^3-Allyl Complex[1]

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The coupling of carbon monoxide molecules is of significance in both synthetic and catalytic organometallic chemistry.[2-11] We have demonstrated that the uranium–carbon multiple bond in $Cp_3U{=}CHPR_3$ reacts with polar, unsaturated systems including carbon monoxide.[1,12] In this communication we report its reaction with $[CpFe(CO)_2]_2$, in which coupling of bridging and terminal carbonyls occurs and a new carbon–carbon bond forms between carbonyl and ylide moieties. Apparently carbon–carbon coupling does not occur by any of the usual, well-documented C–C bond-forming processes.[2-11]

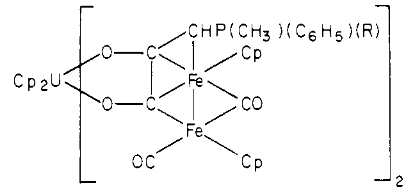
The reaction of equimolar quantities of $Cp_3U{=}CHP(CH_3)(C_6H_5)R$ (**1**) and $[CpFe(CO)_2]_2$ in THF at 25 °C under nitrogen for 8 h produced dark green crystals (**2**) in 45% yield based on phosphorus (eq 1). Cp_4U, identified by NMR, and other incompletely characterized paramagnetic species remain in solution. The ^1H NMR spectra, summarized in Table I, supplementary material, of **2** contain three singlet resonances due to Cp groups, one of which can be assigned as Cp bound to U and the other two as nonequivalent CpFe groups. Additional resonances can be attributed to $CHP(CH_3)(C_6H_5)(R)$ fragments. The infrared spectra of **2a** and **2b** (Table II, supplementary material) contain bands due to both terminal and bridging carbonyls. These data do not provide sufficient information to characterize **2**, thus an X-ray diffraction study was undertaken.

Structures of both **2a** and **2b** were determined and crystal parameters are summarized in Table III, supplementary material.

$Cp_3U{=}CHP(CH_3)(C_6H_5)(R) + [CpFe(CO)_2]_2 \longrightarrow$

1a, R = C_6H_5
b, R = CH_3

Cp = (η^5-C_5H_5)



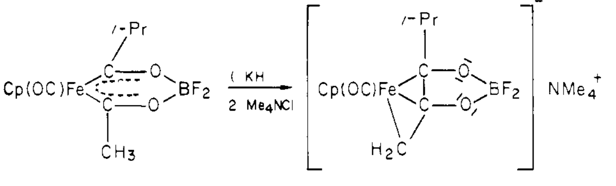
(1)

2a, R = C_6H_5
b, R = CH_3

With the obvious exception of the R group attached to phosphorus, the structures of **2a** and **2b** are very similar. Since a disorder problem exists within one allyl ligand in **2a**, while **2b** is well-behaved, the structural data discussed below are from **2b**.

The molecular structure of **2b** is shown in Figure 1, while structural parameters are summarized in Tables IV and V, supplementary material. The 2.544 (5)-Å Fe(1)–Fe(2) bond length in **2** is very close to the 2.531 (2) Å observed for the Fe–Fe bond in *cis*-$[CpFe(CO)_2]_2$.[13] The distances, C(12)–C(11), 1.34 (3) and, C(11)–C(15), 1.42 (3) Å in the complex organometallic ligands coordinated to Cp_2U are shorter than expected for C–C single bonds, and are consistent with an allyl group. As expected for a delocalized π system the atoms C(11), C(12), and C(15) and their substituents, O(11), O(12), and P and Fe(2), are planar. The distances, Fe(1)–C(11), 2.13 (2), Fe(1)–C(12), 2.05 (2), and Fe(1)–C(15), 2.08 (2) Å are typical for iron η^1:η^3-allyl complexes,[14] and Fe(1) is located 1.46 Å below the allyl plane. The Fe(2)–C(12) distance, 1.96(2) Å, is typical of an η^1 iron vinylcarbene bond.[14] Thus, each of the organoiron ligands derived from a $[CpFe(CO)_2]_2$ molecule contains a newly formed η^1:η^3-allyl created by bond formation between a carbonyl group bonded to iron and $CHPR_3^-$ plus coupling of bridging and terminal carbonyls in the iron dimer.

The mechanism for formation of **2** has not been determined. However, insertion of a terminal carbonyl of $[CpFe(CO)_2]_2$ into the uranium–carbon bond of **1** would be consistent with the known chemistry of **1**.[1,12] The resulting iron enolate carbene intermediate, complex A in Scheme I, could rearrange to B and then undergo ligand exchange to form **2** and Cp_4U. The formation of A and its conversion to B is consistent with the affinity of U(IV) for oxygen,[15] the ability of Cp_3UX compounds to complex hard bases,[16] and the activation of coordinated carbon monoxide by interaction with hard Lewis acids.[17,18] Significantly, the proposed conversion of A to B also closely resembles the transannular coupling that occurs in the reduction of an iron diketonate[19] (eq 2), and similar intermediates can be drawn for both coupling reactions.[20]



(2)

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