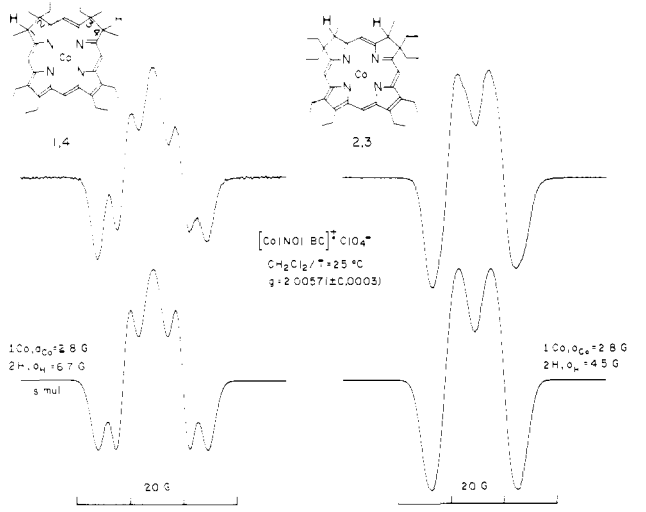

Figure 3. Second-derivative ESR spectra of the radicals obtained on oxidation of the (left) 1,4- and (right) 2,3-dimethyloctaethylisobacteriochlorin complexes of $Co^{II}NO$. The simulations shown under the experimental spectra demonstrate that one cobalt and two protons determine the spectral patterns observed. The proton coupling constants are comparable to those found for the free base and $Fe^{II}(py)CO$ cation radicals of the same macrocycles.[9]

P and C are typical of a π cation in the case of the chlorin[14] and of Fe(III) for the porphyrin. The products obtained by vacuum electrolysis are therefore assigned to $Fe^{III}NO(OEP)^+$, $Fe^{II}NO(OEC)^{+\cdot}$, and $Fe^{II}NO(OEiBC)^{+\cdot}$. The infrared data are consistent with these assignments and suggest that the bent NO bonds are retained in the Fe^{II}iBC and C π cations, and that the NO bond is linear in the Fe^{III}P.[15]

The formation of different P and C products by the two electrolytic methods strongly suggests that traces of water can assist in the displacement of the NO ligands by the ClO_4^- used as electrolyte and that the NO is therefore considerably more "labile" in P and C than in iBC. Use of the iBC framework may thus control the residence time of the substrate at the catalytic site, and the bent vs. linear NO bonds[16] may affect the reactivity of the NO toward the subsequent protolytic reactions[16] that lead to ammonia formation in iBC.

Although the data presented above suggest the existence of C and iBC π cations, the species are ESR silent, presumably because of spin pairing between the radical and the $Fe^{II}NO$. Unlike neutral $Fe^{II}NO$ complexes, $Co^{II}NO$ porphyrins are diamagnetic[8,17] and should yield paramagnetic products upon oxidation. Vacuum electrolysis of the $Co^{II}NO$ complex of 2,3-Me_2(OEiBC)[18] yields an optical spectrum which again resembles an iBC π cation.[9] Its radical nature is evident from its ESR signal (Figure 3), which can be simulated by assuming a small cobalt contribution, a_{Co} = 2.8 G ($I = {}^7/_2$), and two protons, a_H = 4.5 G, i.e., a spin profile characteristic of a_{1u} iBC radicals.[9] To test these assignments, the experiments were repeated with 1,4-Me_2(OEiBC).[18] The resulting ESR signal (Figure 3) requires a_{Co} = 2.8 G and two protons, a_H = 6.7 G, for a satisfactory simulation. The different proton splittings reflect the different spin densities at the inboard and outboard α carbons of the reduced rings and have been observed experimentally and predicted theoretically for other iBC cations.[9]

In accord with the trend observed for the $Fe^{II}NO$ complexes, the $Co^{II}NO$ P, C and iBC complexes all reduce at approximately the same potential: −1.26 to −1.29 V, and become progressively easier to oxidize as the macrocycle is saturated: 0.78 (OEP, irreversible), 0.50 (OEC), and 0.26 V (Me_2(OEiBC)) in butyronitrile. Furthermore, in the case of the iBC radical, the NO also remains bent: ν_{NO} = 1655 and 1695 cm^{-1} for $Co^{II}NO$ 2,3-Me_2(OEiBC)[17] and the radical, respectively, in CH_2Cl_2 (confirmed with ^{15}NO: $\nu_{^{15}NO}$ = 1665 cm^{-1} for the cation).

In conclusion, no obvious differences are observed in the reduction potentials of Fe or Co(II) NO complexes of P, C and iBC that would favor one macrocycle over the others. On the other hand, if electron transport in the enzymic cycle occurs via oxidized macrocycle transients, as previously suggested,[6,9] the iBC macrocycle becomes the easiest to oxidize, the NO substrate is less labile, and its bent conformation perhaps better suited for further reaction. The choice of macrocycle then allows control of oxidation site (metal vs. macrocycle) and of the residence time and reactivity of the NO at the catalytic site.

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(18) 2,3- and 1,4-Me_2(OEiBC) are 3,7-dimethyl-3′,7′-dihydro-2,2′,8,8′,12,13,17,18-octaethylporphyrin and 2,8-dimethyl-2′,8′-dihydro-3,3′,7,7′,12,13,17,18-octaethylporphyrin, respectively. (Chang, C. K. *Biochemistry*, **1980**, *19*, 1971–1976.) We thank Dr. C. K. Chang for samples of the free base compounds. The Co complexes were obtained by refluxing with Co acetate in py under N_2, the py was evaporated and the product washed with H_2O. The NO complexes were prepared in CH_2Cl_2 by addition of NO and EtSH to the CoiBC, followed by vacuum distillation to remove solvent and reagents.

Dependence on Anomeric Configuration of the Temperature Dependence of the Chemical Shifts of Exchangeable Protons of Pyranoses and Pyranosides

Lynn Buffington,* John Crusius, Mark Nachbor, and Linda Reven

Department of Chemistry, Carleton College Northfield, Minnesota 55057

Received June 16, 1983

We report here that the temperature dependence, $\Delta\delta/\Delta T$, of the proton NMR chemical shifts of the exchangeable protons of some pyranosides is a function of anomeric configuration. The significance of this finding is twofold: (1) for its bearing upon the well-known anomeric effect and exo-anomeric effect,[1] and (2) for its importance to those using $\Delta\delta/\Delta T$ values as indicators of conformation in carbohydrates of biological significance. While our study is far from exhaustive it suggests the following: (1) In dimethyl sulfoxide (Me_2SO) solutions the exchangeable proton $|\Delta\delta/\Delta T|$ values of substituents at carbon 2 are greater for α anomers than for β anomers while those of substituents at carbon 1 are greater for β anomers than for α anomers. (2) Exchangeable protons of both hydroxyl and acetamide ($NHCOCH_3$) substituents are affected.

The chemical shifts (δ) of exchangeable protons in solvents such as Me_2SO and H_2O generally decrease with increasing temperature. This is attributed to the disruption of hydrogen bonding (involvement of a proton in a hydrogen bond causes a shift to greater δ values).[2] When the interaction being disrupted is with one of these solvents, a large dependence on temperature indicates a conformation in which the proton is exposed to the solvent; a small dependence corresponds to a proton shielded from the

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Table I. $\Delta\delta/\Delta T$ Values (ppb/deg) in Me_2SO

compd[a]	α amide H	β amide H	α C-2 OH	β C-2 OH	α C-1 OH	β C-1 OH	α C-6 OH	β C-6 OH
A (0.15 M)[b]	−7.5	−3.8			−5.2	−6.2	−6.9	−6.8
B (0.01 M)	−7.1[c]						−6.3	
B (0.94 M)	−7.8						−6.5	
C (<0.02 M)		−4.7[d]						
D (0.08 M)		−4.9						−7.0
E (0.10 M)[b]	−6.9	−3.3		(−4.0, −6.2)[e]	−5.4	−6.4		−6.8
F (0.11 M)			−8.7[c]				−7.4[c]	
G (0.12 M)				−7.5				−6.4
H (0.17 M)			(−6.4, −6.4, −7.4)[e]				−5.6	
I (0.14 M)				(−6.5, −7.6, −7.8)[e]				−5.4
J (0.006 M)			−7.7		−5.7		−6.8	
J (0.17 M)			−7.8		−5.8		−6.9	
K (0.006 M)				(−6.2, −7.0)[e,f]		−6.2[c]		−6.7
K (0.21 M)				(−6.3, −6.9)[e,f]		−6.3		−6.8

[a] Names of compounds given in ref 11. [b] Mixture of anomers. [c] Maximum deviation between observed and calculated frequencies was greater than digital resolution. In F the average deviation was twice digital resolution; in B and K the average deviation was less than digital resolution. [d] Amide substituent at C-2. [e] Parentheses indicate incomplete assignment of hydroxyls. In H, for example, three $\Delta\delta/\Delta T$ values were measured, but we do not know which corresponds to C-2 OH, C-3 OH, or C-4 OH. [f] Temperature dependences are reported for two of three overlapping incompletely assigned hydroxyl signals. Overlap prevented determination of the third $\Delta\delta/\Delta T$ value.

solvent. Use of $\Delta\delta/\Delta T$ values of peptide and carbohydrate protons are found in the literature.[3-6]

The results of our measurements are summarized in Table I. The values of $\Delta\delta/\Delta T$ are the slopes, a, from a linear least-squares fit of data to $\delta = aT + b$. Maximum deviations of calculated frequencies from expected frequencies were comparable to the digital resolution of the measurement except where noted. NMR spectra were obtained on a Bruker HX 270-MHz instrument equipped with a temperature controller. Chemical shifts were referenced with respect to internal Me_4Si or DSS[7] and were measured at five temperatures in the range 295–320 K. Temperature calibration was checked by using ethylene glycol.[8] Spectra in H_2O were obtained by the WEFT technique.[9] Resonances were assigned from the literature[10] and/or from standard decoupling experiments. All compounds were obtained from commercial sources and are referred to by Roman letter designations.[11]

The difference between α and β anomer $|\Delta\delta/\Delta T|$ values was most pronounced for the exchangeable protons of acetamide substituents (amide H, Table I), with α anomer values of about 7 ppb/deg and β anomer values of about 4 ppb/deg. Somewhat surprisingly, the pair of amide $\Delta\delta/\Delta T$ values in E, a compound with the acetamide substituent at carbon 3, were very similar to those for A–D, compounds with acetamide substituents at carbon 2, one carbon closer to the anomeric center.

For protons of hydroxyl substituents at carbon 2 the α $|\Delta\delta/\Delta T|$ values were about 1 ppb/deg greater than the β $|\Delta\delta/\Delta T|$ values for the sugars of the gluco configuration (F and G, J and K, Table I); lack of assignments prevents evaluation of whether a similar relation holds for the pair of galacto sugars (H and I, Table I).

Table II. δ and $\Delta\delta/\Delta T$ Values as a Function of Solvent

	H_2O[b]		Me_2SO		HFIP	
proton[a]	δ[c]	$\Delta\delta/\Delta T$[d]	δ[c]	$\Delta\delta/\Delta T$[d]	δ[c]	$\Delta\delta/\Delta T$[d]
amide of A (α)[e]	8.05	−9.0	7.65	−7.5	6.57	−3.5[f]
amide of A (β)[e]	8.16	−8.3	7.77	−3.8		
amide of B (α)	8.07	−9.1	7.74	−7.4	6.46	−4.3[f]
amide of C (β)[g]	8.17	−7.4	7.85	−4.7		
amide of D (β)			7.67	−4.9	6.55	

[a] Letters refer to compounds as designated in ref 11. [b] Preliminary results show that both δ and $\Delta\delta/\Delta T$ vary somewhat with pH; pH's were as follows: A, 3.5; B, 1.7; C, 2.1. [c] ppm at 27 °C. [d] ppb/deg. [e] Anomeric mixture. [f] Data consisted of three rather than five points. For B, average deviation between calculated and observed frequencies was less than digital resolution. For A, this average deviation was twice the digital resolution. [g] Values are for amide substituent at C-2.

For protons of carbon 1 hydroxyl substituents the β $|\Delta\delta/\Delta T|$ values were 0.5 to 1 ppb/deg greater than the α $|\Delta\delta/\Delta T|$ values (A, E, J and K, Table I).

The $|\Delta\delta/\Delta T|$ values increase slightly with increasing sugar concentration (B, J, K, Table I). Evidently intermolecular interactions are a factor in the observed $\Delta\delta/\Delta T$ values. However, solute–solvent interactions are of major importance as the variation of $\Delta\delta/\Delta T$ values with solvent indicates (A, B, C in Me_2SO, H_2O, and hexafluoroisopropanol (HFIP), Table II). To the extent to which the $|\Delta\delta/\Delta T|$ values reflect the effect of temperature in the disruption of solute–solvent hydrogen bonds we would expect the protons with larger $|\Delta\delta/\Delta T|$ values to be those that are more strongly hydrogen bonded with the solvent. The $|\Delta\delta/\Delta T|$ values decrease from maximum values in H_2O, through Me_2SO, to minimum values in HFIP (Table II). These results are as expected for solvent-exposed exchangeable protons, since H_2O is a good hydrogen-bond donor and acceptor,[12] Me_2SO is a good hydrogen-bond acceptor, and HFIP is a poor hydrogen-bond acceptor. Changes in δ with solvent are also as expected; that is, they too decrease in the order $H_2O > Me_2SO >$ HFIP (Table II).[13]

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(11) A, 2-acetamido-2-deoxy-D-glucopyranose; B, methyl 2-acetamido-2-deoxy-α-D-glucopyranoside; C, 1-(L-aspartamido)-2-acetamido-1,2-dideoxy-β-D-glucopyranoside; D, 1-amino-2-acetamido-1,2-dideoxy-β-D-glucopyranoside; E, 3-acetamido-3-deoxy-D-glucopyranose; F, methyl α-D-glucopyranoside; G, methyl β-D-glucopyranoside; H, methyl α-D-galactopyranoside; I, methyl β-D-galactopyranoside; J, α-D-glucopyranose; K, β-D-glucopyranose.

(12) It has been suggested that a hydrogen bond with a sugar hydroxyl acting as a donor and H_2O as an acceptor is strengthened by that same sugar hydroxyl simultaneously serving as an acceptor in a hydrogen bond with H_2O.[6] It has also been suggested that in amides two hydrogen-bonding interactions contribute to downfield shifting of the amide[3a] proton: (1) the amide group serving as a hydrogen-bond donor through the amide proton and (2) the amide group serving as an acceptor through the carbonyl oxygen.

(13) The δ values and the interpretation in terms of hydrogen-bonding properties of the solvent are consistent with the greater value of δ of glucose hydroxyl protons in H_2O relative to Me_2SO,[6] with the greater value of δ for tetrapeptide amide protons in H_2O relative to Me_2SO[14] and with the greater value of δ of peptide and *N*-methylacetamide amide protons in Me_2SO relative to HFIP.[15]

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.

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Enforced Deformation of Porphyrins by Short-Strap Bridging

Tilak P. Wijesekera, John B. Paine III, and David Dolphin*

Department of Chemistry
The University of British Columbia
Vancouver, British Columbia, Canada V6T 1Y6

Frederick W. B. Einstein* and Terry Jones

Department of Chemistry, Simon Fraser University
Burnaby British Columbia, Canada V5A 1S6

Received February 22, 1983

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

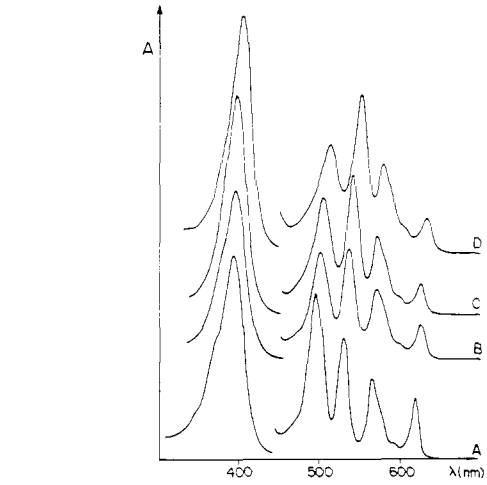
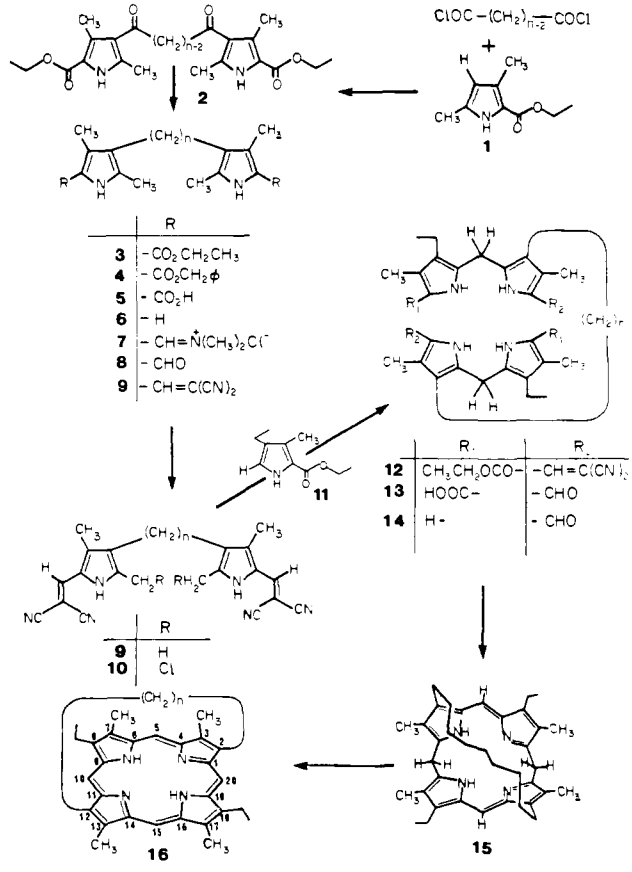


Figure 1. Optical spectra (CH_2Cl_2) of (A) etioporphyrin II, (B) **16**, n = 11, (C) **16**, n = 10, and (D) **16**, n = 9.

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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