that are assembled in Table I, together with the corresponding values of δ_H and δ_{SA}.

The second investigation involved an attempt to unravel and rationalize the interacting effects that contribute to critical temperatures, CT, and boiling points, bp, of nondipolar and dipolar compounds. We defined a polarizability term, N', by eq 4, where

$$N' = N + 3N_{Cl} + 3N_{Br} - N_F + 3N_{DB} + 8 \text{ (for cycloalkanes)} + 6.0\,(3.0 - \mu) \text{ (for aromatics)} \quad (4)$$

N is the total number of atoms in the molecule, N_{Cl}, N_{Br}, N_F, and N_{DB} are the numbers of chlorine, bromine, and fluorine atoms and double bonds, and μ is the gas-phase electric dipole moment.[4] We then showed that the CT and bp of a large number of nondipolar and dipolar compounds were well correlated by eq 5 and 6.[5] A plot of $\mathrm{CT_{exptl}}$ vs. $\mathrm{CT_{calcd}}^{\mathrm{eq\ 5}}$ is shown in Figure 1.

$$\mathrm{CT\ (K)} = -99.9 + 26.6(M_r)^{1/2} + 78.9(N')^{1/2} + 20.3\mu^2 \qquad n = 48,\ r = 0.993,\ \mathrm{SD} = 22.1\ \mathrm{K} \quad (5)$$

$$\mathrm{bp\ (K)} = -86.6 + 17.7(M_r)^{1/2} + 56.1(N')^{1/2} + 13.5\mu^2 \qquad n = 48,^5\ r = 0.994,\ \mathrm{SD} = 13.4\ \mathrm{K} \quad (6)$$

We then defined by eq 7 and 8 two quantities $(\Delta\Delta\mathrm{CT})_{SA}$ and $(\Delta\Delta\mathrm{bp})_{SA}$, which are the increments caused by self-association of the ROH compounds. The $(\Delta\Delta\mathrm{CT})_{SA}$ terms correspond to

$$(\Delta\Delta\mathrm{CT})_{SA} = \mathrm{CT_{exptl}} - \mathrm{CT_{calcd}}^{\mathrm{eq\ 5}} \quad (7)$$

$$(\Delta\Delta\mathrm{bp})_{SA} = \mathrm{bp_{exptl}} - \mathrm{bp_{calcd}}^{\mathrm{eq\ 6}} \quad (8)$$

the vertical displacements of the ROH data points from the regression line in Figure 1. Values of the ΔΔ terms are also assembled in Table I.

If the ΔΔ terms and the δ_{SA} terms all depend on the ROH self-association energies, they might be expected to bear simple relationships to one another. This is, indeed, the case, the three sets of properties showing very nice linear regressions (eq 9–11).

$$(\Delta\Delta\mathrm{CT})_{SA}\ \mathrm{(K)} = -83.3 + 2.086(\Delta\Delta\mathrm{bp})_{SA} \qquad r = 0.998,\ \mathrm{SD} = 8.6\ \mathrm{K} \quad (9)$$

$$(\Delta\Delta\mathrm{CT})_{SA}\ \mathrm{(K)} = -68.5 = 93.9\delta_{SA} \qquad r = 0.998,\ \mathrm{SD} = 6.3\ \mathrm{K} \quad (10)$$

$$(\Delta\Delta\mathrm{bp})_{SA}\ \mathrm{(K)} = 7.8 + 44.7\delta_{SA} \qquad r = 0.995,\ \mathrm{SD} = 6.1\ \mathrm{K} \quad (11)$$

It is of interest that eq 11 has a smaller intercept than the standard deviation of antecedent eq 6, suggesting a direct proportionality. That this is not the case with eq 9 and 10 may be because the bp are all at the same pressure, but the CT are at different critical pressures.

We were also interested in examining how the ΔΔ and δ_{SA} values compared with other properties that depend on extents of self-association, but such information is quite sparse in the literature. The most informative study is by Abboud and co-workers,[6] who have reported the following dimerization constants, K_d, in cyclohexane solvent: *t*-BuOH, 22; *i*-PrOH, 39; *n*-PrOH, 47; EtOH, 48; MeOH, 56.[7]

Abboud and co-workers[6] also observed that their association constants seemed to depend primarily on the steric influence of R and hence were well correlated with Taft's steric parameter, E_s.[8] Accordingly we have also carried out correlations of the ΔΔ terms with the E_s values of R in ROH, and we have found the linear fits to be quite good (eq 12 and 13).

$$(\Delta\Delta\mathrm{CT})_{SA}\ \mathrm{(K)} = 172.6 + 211.0E_s \qquad r = 0.989,\ \mathrm{SD} = 18.6\ \mathrm{K} \quad (12)$$

$$(\Delta\Delta\mathrm{BP})_{SA}\ \mathrm{(K)} = 123.0 + 102.0E_s \qquad r = 0.981,\ \mathrm{SD} = 11.6\ \mathrm{K} \quad (13)$$

On the above basis we conclude that the δ_{SA} terms are convenient measures of extents of self-association of amphiprotic solvents. We also suggest that for solution studies (or polymer swelling studies) δ_C is a more appropriate measure of the cavity term than δ_H.

Registry No. 1-Butanol, 71-36-3; 2-propanol, 67-63-0; 1-propanol, 71-23-8; ethanol, 64-17-5; methanol, 67-56-1; water, 7732-18-5.

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[4] For a number of compounds of different polarizability classes, $N' - N$ was found to be linear with $(n^2 - 1)/(2n^2 + 1)$ with a correlation coefficient of 0.989.

[5] Dimethylformamide and dimethylacetamide are two important solvents that do not fit eq 6. We will discuss possible reasons in the full paper.

[6] Frange, B.; Abboud, J.-L. M.; Benamou, C.; Bellon, L. *J. Org. Chem.* **1982**, *47*, 4553.

[7] They also concluded that tetramerization (K_{dd} for dimerization of dimers) is over an order of magnitude more important than dimerization. For the couple MeOH/*t*-BuOH in CCl_4, they found the ratios of K_d and K_{dd} values to be 1.83 and 3.49, respectively.

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Models for Nitrite Reductases. Redox Chemistry of Iron Nitrosyl Porphyrins, Chlorins, and Isobacteriochlorins and π Cation Radicals of Cobalt Nitrosyl Isobacteriochlorins

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Nitrite reductases catalyze the multielectron reductions of nitrite to ammonia or to nitric oxide.[1,2] The identification of iron isobacteriochlorins (sirohemes) and chlorins (hemes d) as the prosthetic groups of these enzymes[1,2] and the detection of $\mathrm{Fe^{II}NO}$ complexes in the catalytic cycles of both types of nitrite reductases[3] prompted us to investigate the redox chemistry of $\mathrm{Fe^{II}NO}$ complexes of porphyrins (P), chlorins (C), and isobacteriochlorins (iBC). We find that the potentials for the one-electron reductions of these complexes are independent of macrocycle and thus offer no obvious advantage for biological selection among the three macrocycles. However, the progressive saturation of the macrocycles makes their $\mathrm{Fe^{II}NO}$ complexes easier to oxidize, which results in π cation radical rather than Fe(III) formation, and renders the NO substrates considerably more labile when bound to oxidized Fe porphyrins than to isobacteriochlorins.

We have extended these studies to $\mathrm{Co^{II}NO}$ complexes and demonstrate unambiguously the formation of $\mathrm{Co^{II}NOiBC}$ π radicals. These results may themselves be biologically relevant because some sulfite reductases utilize cobalt iBCs to catalyze electron transport[4] and because sulfite reductases also reduce nitrite.[1]

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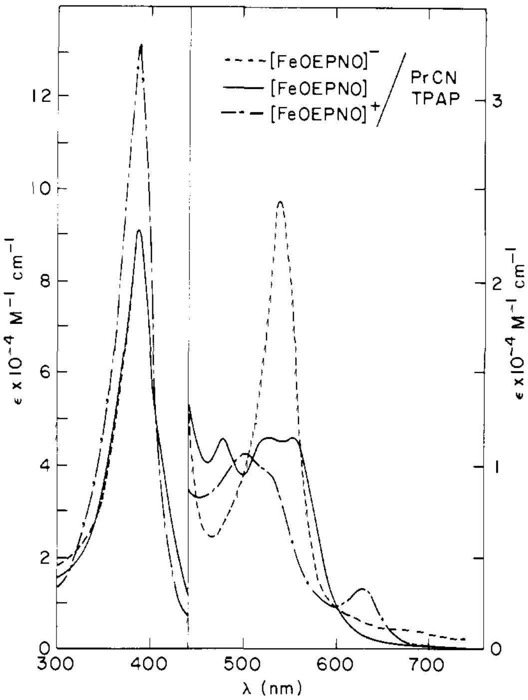

Figure 1. Optical absorption spectra, in butyronitrile, of iron(II) nitrosyl octaethylporphyrin (—), its one-electron reduction product (- - -), and its one-electron oxidation product (— - —). The counter ions are tetrapropylammonium and perchlorate for the reduced and oxidized species, respectively.

The NO infrared stretches for the Fe^{II}NO complexes of all three macrocycles[5] are found at 1670 cm^{-1} in Nujol, indicating the same bent Fe–NO bonds.[7,8] Similarly, all three complexes exhibit the same 3-line ESR spectra,[8] with a_N = 16.2 G in toluene solution, again suggesting no significant differences in the binding of the NO to the Fe(II).

The Fe^{II}NO complexes display reversible cyclic voltammetric reduction at effectively the same potential: −1.08 (OEP), −1.08 (OEC), and −1.11 (OEiBC) V in butyronitrile (vs. SCE). This insensitivity to the nature of the macrocycle is typical of metal-centered reductions.[6,9] Indeed, extended Hückel calculations by Hanson[10] suggest that the electron adds to a hybrid Fe–NO orbital. The complexes of all three macrocycles can be reversibly reduced and reoxidized, in a vacuum electrolysis cell,[11] to yield the optical spectra shown in Figures 1 and 2.[12] As the reductions proceed, the typical Fe^{II}NO ESR signals diminish, and the reduced products are ESR silent.

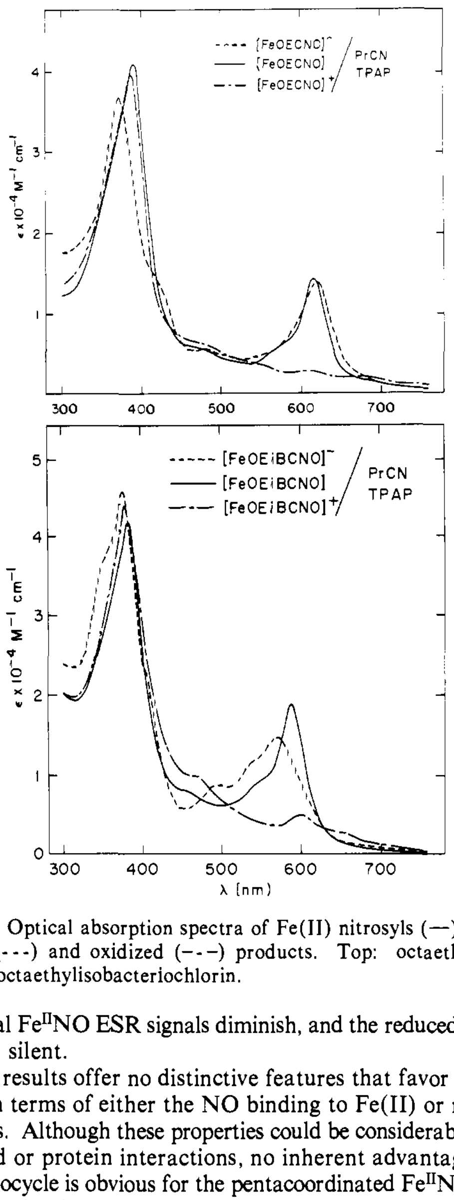

Figure 2. Optical absorption spectra of Fe(II) nitrosyls (—) and their reduced (- - -) and oxidized (— - —) products. Top: octaethylchlorin; bottom: octaethylisobacteriochlorin.

These results offer no distinctive features that favor iBC over C or P in terms of either the NO binding to Fe(II) or reduction potentials. Although these properties could be considerably altered by ligand or protein interactions, no inherent advantage of any one macrocycle is obvious for the pentacoordinated Fe^{II}NO species or their reduction.

In contrast to the invariance observed on reduction of the Fe^{II}NO complexes, the compounds undergo progressively easier, reversible oxidation: $E_{1/2}$ = 0.63 (OEP),[13] 0.48 (OEC), and 0.22 (OEiBC) V in butyronitrile. This trend parallels the oxidation potentials of free base and zinc P, C, and iBC where electron abstraction occurs from the π system[6,9] and of iron(II) pyridine CO complexes, where oxidation of P and C leads to Fe(III) and loss of CO but that of iBC results in an Fe^{II}(py)CO π cation.[9] Controlled potential electrolyses, under nitrogen,[11] of the three Fe^{II}NO complexes yield optical spectra that confirm the reported[12] generation of Fe^{III}PClO$_4$ and establish that Fe^{III}CClO$_4$ is similarly formed. However, oxidation of Fe^{II}NOiBC leads not to Fe^{III}ClO$_4$ but to a species with an optical spectrum similar to those of Fe^{II}iBC π cations.[9] Electrooxidations in vacuo resulted in the optical spectra shown in Figures 1 and 2.[12b] Reduction of the oxidized species yielded better than 95% of the parent compounds, thus establishing that the NO ligands were not lost. Infrared measurements in Nujol further confirmed the presence of NO in the oxidized products: ν_{NO} = 1830 (P), 1705 (C), and 1680 (iBC) cm^{-1}. (A weak band at 1765 cm^{-1} for iBC is attributable to an impurity.) The optical spectrum of the oxidized iBC is identical with that obtained by oxidation under N$_2$, whereas those of the

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[5] The three macrocycles are the dianions of 2,3,7,8,12,13,17,18-octaethylporphyrinato (OEP), 7′,8′-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinato (OEC), and 2′,3′,7′,8′-tetrahydro-2,3,7,8,12,13,17,18-octaethylporphyrinato (OEiBC) and were prepared as described by Stolzenberg et al.[6] Fe(OEP)Cl was reduced with NaBH$_4$, and NO was introduced to form Fe^{II}(OEP)NO, Fe(OEC) and Fe(OEiBC)NO were prepared by reduction of (Fe(OEC))$_2$O and Fe(OEiBC)Cl with MeSH and NH$_3$ in benzene followed by addition of NO. The compounds were obtained as solids by vacuum distillation of the solvent and reagents and were handled under vacuum.

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[13] The $E_{1/2}$ value for OEP is similar to those reported previously: ref 12 and: Buchler, J. W.; Kokisch, W.; Smith, P. D.; Tonn, B. *Z. Naturforsch., B* **1978**, *33B*, 1371–1380.

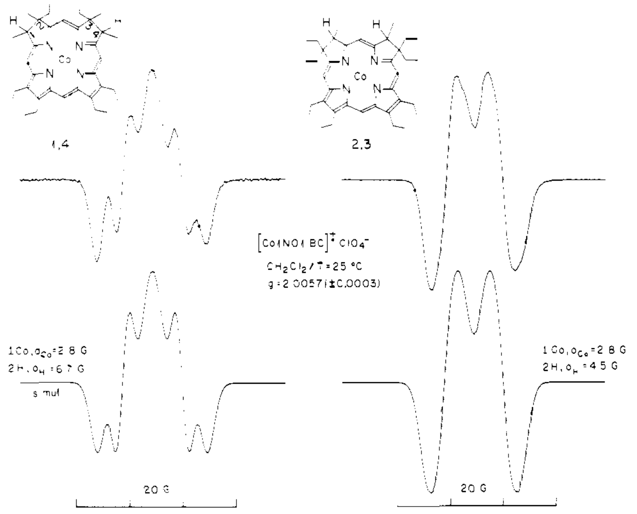

Figure 3. Second-derivative ESR spectra of the radicals obtained on oxidation of the (left) 1,4- and (right) 2,3-dimethyloctaethylisobacteriochlorin complexes of Co^{II}NO. The simulations shown under the experimental spectra demonstrate that one cobalt and two protons determine the spectral patterns 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: $\nu_{NO} = 1655$ 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.

Acknowledgment. We thank Drs. I. Fujita and A. R. Newman for their assistance in some phases of this work and Drs. L. K. Hanson, K. M. Kadish, and W. R. Scheidt for communicating their results prior to publication. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016.

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(17) Nitrosyl-5,10,15,20-tetraphenylporphinatocobalt(II) (Co(TPP)NO) is diamagnetic. An X-ray structure shows the NO to be bent with $\nu_{NO} = 1689$ cm^{-1} in KBr. Scheidt, W. R.; Hoard, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8281-8286.

(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$_2$O. The NO complexes were prepared in CH$_2$Cl$_2$ 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

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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$_2$SO) 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$_2$SO and H$_2$O 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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