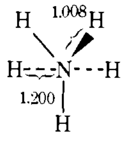
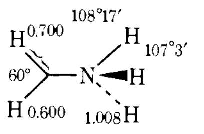
Pauling, considering the electronegativities of nitrogen and hydrogen, concluded that the charge distribution in NH_4^+ is about equal over the five atoms.[9] Thus considering the charge effects in the reaction competing attack of the nucleophile on nitrogen seems possible. We also carried out CNDO/2 calculations for the possible limiting D_{3h} and C_s structures of nitrogen pentahydride to minimize the binding energy by varying bond lengths. The calculated heats of formations for these forms are as shown. The trigonal bipyramidal form is favored by some 41 kcal/mol over the C_s symmetry form, as is found in calculations of CH_5^- (in the latter case the larger charge-charge repulsion effect caused a calculated difference of 55 kcal/mol). Further we also calculated the comparative species with hydride attack colinearly on hydrogen



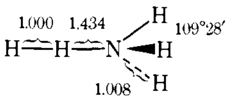
D_{3h}

$\Delta H_f = -613$ kcal/mol



C_s

$\Delta H_f = 572$ kcal/mol

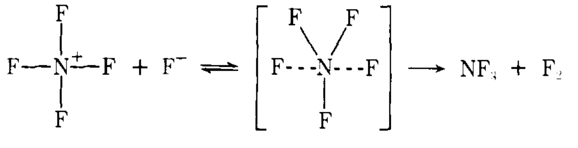


$\Delta H_f = 666$ kcal/mol

The data show that a nucleophilic attack on hydrogen by hydride ion is favored. Even though the calculations seem to favor largely the attack on hydrogen by the hydride ion, the alternative attack on nitrogen cannot be dismissed in view of the experimental facts. One of the possible explanations for the lowering of the barrier in the latter mechanism is the participation of another NH_4^+ molecule which can help the process by providing a proton for the removal of the otherwise unstable displaced hydride ion.

Uncertainties in the geometries used in the calculations and the applicability of the CNDO/2 method to this system could account for the calculated large differences between attack on hydrogen and nitrogen.

In related studies we observed that the known $NF_4^+SbF_6^-$ salt[10] when treated with LiF decomposed to NF_3, F_2, and $LiSbF_6$. This reaction could further indicate the possibility of nucleophilic attack by F^- on nitrogen, as the high electronegativity of fluorine would enhance this mode over attack on fluorine. Whether there is fluorine exchange must await contemplated studies using $^{18}F^-$.



Our present work showing the involvement of pentacoordinated NH_5 in the nucleophilic displacement of the ammonium ion by hydride ion through attack on the quaternary nitrogen opens up of what is considered a new interesting field of nucleophilic displacement reactions on quaternary nitrogen. We are continuing related studies including investigations of such reactions as the nucleophilic displacement of ammonium (including anilinium) ions by nitrite ion, i.e., the nucleophilic analog of the diazotization reaction.

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Solvent Effect on the Magnetic Anisotropy of Low-Spin Dicyano Ferric Complexes of Natural Porphyrins

Sir:

The environment of the prosthetic group in hemoproteins plays a crucial role in modulating the redox and oxygen-binding properties at the central metal ion. The discussion of the spectral and magnetic properties of hemoproteins and their model compounds usually assumes a well-defined electronic structure for the prosthetic group.[1-4] Recent work has shown[2-4] that certain structure-function relationships of hemoproteins can be conveniently studied using the isotropic shift of peripheral porphyrin substituents in the hemoproteins or in model compounds. Although changes in the NMR shifts either within the protein or on going from the model compound to the protein have been interpreted in terms of structural changes in the heme environment,[2-4] to date no explicit recognition has been given to the possible effect of solvation on the electronic structure of the iron. Contrary to earlier indications,[5] we find that the proton NMR, and hence by inference the electronic structure, of low-spin dicyano ferric porphyrins are not only sensitive to the solvent but depend on solvent in a characteristic manner which suggests that solvation should be considered in interpreting changes in the NMR spectra of cyano hemoproteins.[2-4]

Table I presents the chemical shifts[6] for several ring substituents in dicyano complexes of natural porphyrins in various solvents.[7] The shifts change monotonically with solvent, with *all* positions experiencing an overall downfield bias moving up the table. The ring substituent shifts in low-spin ferric porphyrins have been shown to arise from upfield dipolar shifts and π-contact shifts reflecting L → M π charge transfer.[8,9] The changes in shifts with solvent, however, can be shown to reflect primarily changes in the dipolar shift (magnetic anisotropy). This is illustrated in Table II, where the shift changes for various functional groups parallel the calculated relative geometric factors.[8,9] Changes in the ex-

Table I. Chemical Shifts for Selected Resonances of Dicyano Ferric Porphyrin[a] Complexes

Solvent	E_T[b] (kcal mol^{-1})	H bond donor ability	Shifts from TMS (ppm) CH$_3$[c]	α-CH$_2$[c]	α-vin[c]	Pyrrole-H[c,d]
D_2O[e]	63.1	Good	−19.5	−8.8	−14.5	+13.7
CD_3OD	55.5	Fair	−16.5	−7.5	−13.4	+15.2
$CDCl_3$[f]	39.1	Poor	−16.0	−5.8	−11.4	+17.5
CD_2Cl_2[f]	41.1	None	−15.1	−5.7	−11.1	+18.2
DMSO	45.0	None	−15.0	−5.7	−10.4	+17.7

[a] All data from protoporphyrin IX dimethyl ester Fe^{III}Cl + KCN except as noted. [b] Solvent polarity. C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 4, 29 (1965). [c] Lowest field resonance for substituent. [d] From deuteroporphyrin IX Fe^{III}Cl + KCN. [e] From protoprophyrin IX Fe^{III}Cl + KCN. [f] Cyanide added as tetra-*n*-butylammonium cyanide.

Table II. Solvent Shift for Mean Substituent Resonance and Relative Geometric Factors for Dipolar Shifts[a]

	Pyrrole substituent[a] H	CH$_3$	α-CH$_2$	α-vin	β-CH$_2$	β-vin
Relative geometric factor[b]	(−4.2)	−3.0	−3.0	−3.0	−2.0	−2.0
Solvent shift[c] (ppm)	−4.2	−4.0	−3.1	−4.0	−2.3	−1.3

[a] Average of all shifts for a given type of substituent proton; for protoprophyrin IX Fe^{III}Cl + KCN except for H. [b] Normalized to H shift in deuteroporphyrin IX Fe^{III}Cl + KCN. [c] $\delta_{D_2O} - \delta_{DMSO}$.

tent of π spin transfer will cause shift changes in opposite directions for pyrrole proton and methyl groups.[8,9]

The change in dipolar shifts indicates substantial variation in magnetic anisotropy; for $CDCl_3$ the shifts are consistent with $g_\parallel \simeq 1.8$, $g_\perp \simeq 3.6$,[2,8] while in D_2O $g_\parallel \simeq 2.0$, $g_\perp \simeq 2.9$[9] are appropriate. The changes in shifts do not correlate well with either dielectric constant or polarity (E_T value) but do parallel the hydrogen bonding donor strength of the solvent, as shown in Table I. A similar study of bisimidazole complexes reveals that such a large bias of the shifts with solvent is absent, suggesting that the site of the specific solvation interaction is the axial ligand rather than at the porphyrin core or substituents.[10]

Coordinated cyanide is known to function as a Lewis base,[11] so it is reasonable to expect it to act as an H-bond acceptor. Since protonation of coordinated cyanide decreases its σ-basicity while increasing its π-acidity toward the metal ion,[11] increased H bonding will weaken the axial ligand field. In D_2O the cyanide ligand field has been reduced to yield a magnetic anisotropy comparable to the bisimidazole complex.[9,12] The increased π-acidity of cyanide in D_2O should facilitate porphyrin → metal π bonding. Detailed analysis of the shifts in Table II reveals that the deviation from quantitative agreement between shifts changes and relative geometric factors can be rationalized by the expected small increase in the π spin density in the pyrrole ring. The failure of the meso protons to follow the solvent effect (observed solvent shift −1.0 ppm, calculated relative geometric factor −7.1) presumable results from the previously postulated[9] presence of some σ, as well as π spin density, at the meso carbons.

These results demonstrate the important perturbation of the electronic structure which can arise from solvation effects and bring into question the applicability of solid-phase, low-temperature EPR results[2,8,9,12,13] on cyano ferric hemes for describing the ambient-temperature solution electronic structure. Preliminary work has shown[14] that similar changes in shifts are observable in the mixed cyano-imidazole complexes which are better models for the hemoprotein NMR work. It has been postulated that H-bonding occurs between axial ligands and the distal histidine in several metmyoglobin and hemoglobin complexes.[15] This interaction has been suggested as the probable cause of a bent carbonyl ligand in insect myoglobin.[16] With cyanide at the distal site, the porphyrin substituent shifts may turn out to be useful probes for the interaction with the distal histidine. More complete characterization of the effect in both model compounds and myoglobin complexes is in progress.

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