it confirms the molecular localized nature of the magnetic excitations.

The differences between observed and theoretical $\vec{Q}$ dependencies (vide supra) may have three principal physical origins: (i) underlying phonon scattering, (ii) multiple scattering, and (iii) intermolecular interactions. We cannot rule out a contribution from (i). The high concentration of hydrogen atoms in the sample (8 H per 1 Ni) is mainly responsible for multiple scattering. Due to the extremely high incoherent nuclear scattering amplitude of hydrogen, a large portion of the incoming neutrons are scattered incoherently by hydrogen atoms before they reach a magnetic center. As a result the neutrons interacting with the magnetic centers do not all have the same wave vector, $\vec{Q}$ is no longer well defined, and relation 4 becomes soft. A quantitative estimate of these effects is difficult. We feel that it accounts for at least part of the observed discrepancies.

Deviations from theoretical Q dependencies may also arise through intermolecular interactions (short-range order). If, instead of one nickel dimer, we consider a pair of dimers with weak interaction between them, there will be some INS intensity depending on cos $(\vec{Q}\cdot\vec{R}_{id})$, where $\vec{R}_{id}$ is the shortest interdimer Ni–Ni vector. The relative magnitude of that intensity should, however, be small.

Returning to the magnetic properties, we can now interpret the inflection of the low-temperature magnetization as a result of intermolecular interactions, since the intramolecular splitting pattern corresponds to the left-hand side of Figure 2. Using the molecular field approach described in section 3, i.e., assuming the molecular field to be induced by the magnetization resulting from the external magnetic field, we can calculate magnetization curves for various values of J'.

Sigmoidal curves are obtained for $T < 2.5$ K and J' around -0.25 cm^{-1}, and they give a good reproduction of the experimental data (Figure 4). A literature value of $g = 2.25$ (isotropic) was used, and no attempt was made to get the best fit to the data by varying both J' and g. The observed differences of low-temperature magnetizations between N-deuterated and undeuterated $[Ni_2(en)_4Br_2]Br_2$ are very small. Due to the strong temperature dependence of the effects they may have an experimental and not a physical origin.

For comparison purposes we attempted to determine the relevant parameters from the temperature dependence of the magnetic susceptibility. As it is impossible to extract five parameters from the data in Figure 3, we fixed $g = 2.25$ (literature) and $E = 0$ (from INS). The following values were then obtained from the least-squares fit: $J = 4.0$ cm^{-1}, $D = -6.0$ cm^{-1}, $J' = -0.4$ cm^{-1}. The agreement with the INS values is reasonable. It is undoubtedly somewhat fortuitious (cf. Table I) because the "correct" values were used as starting parameters and also partial use of the INS results ($E = 0$) was made.

The low-temperature magnetization measurements (Figure 4) are a much more sensitive probe of the intermolecular interactions than is the magnetic susceptibility. Therefore, the J' value determined from the magnetizations is more trustworthy. A comparison of the parameters determined in this study with those of related systems shows J to be well within the range of exchange parameters reported for di-μ-bromo and di-μ-chloro bridged species.[4,2,16] The ferromagnetic sign can be rationalized in terms of Kanamori–Goodenough rules or more sophisticated theoretical models. $|D|$ values reported for mononuclear nickel(II) complexes range from 0 to 6 cm^{-1}.[17] Values of up to 22 cm^{-1} have been proposed on the basis of heat capacity and magnetic susceptibility measurements for the linear chain compounds NiX_2L_2 (X = Cl, Br; L = pyridine, pyrazole).[2b] Both sign and magnitude of J' appear reasonable.

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Proton Magnetic Resonance Studies on High-Spin Iron(III) Porphyrins

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Results of isotropic proton magnetic resonance studies on a series of high-spin five-coordinated (tetraphenylporphinato)iron(III) complexes, Fe(TPP)X (X = NCS, Cl, Br, I), have been reported. Measurements have been done at 270 MHz in $CDCl_3$ solution between 238 and 328 K. The temperature-dependent isotropic shifts show increasing deviation from $1/T$ dependence from X = NCS to I. Further, the isotropic shifts for the phenyl protons show certain anomalies in sign and magnitude. These observations have been rationalized in terms of large dipolar shifts, which have been very accurately determined in the present work by using our experimental values of single-crystal susceptibility data. The dipolar-shift contribution is, as expected, quite large for the phenyl protons but is also significant for the pyrrole protons, being about 18% of the total shift for Fe(TPP)Br at 238 K. The contact shift for the phenyl protons, though much smaller in magnitude than that of the pyrrole protons, is however not insignificant and constitutes about half of the total shift. An analysis of the isotropic shift data using the theory of Kurland and McGarvey gives accurate values for the hyperfine coupling constants of these high-spin molecules and suggests that the zero-field splitting of the $^6A_1$ ground state is nearly the same in the solid as in the chloroform solution.

Introduction

Proton magnetic resonance studies on synthetic iron(III) porphyrins have been very useful in understanding and assigning the more complex NMR spectra of heme proteins.[1–3] These studies have also helped in understanding the nature of the metal–ligand bonding and the distribution of unpaired-electron spin density across the porphyrin skeleton.[4–6]

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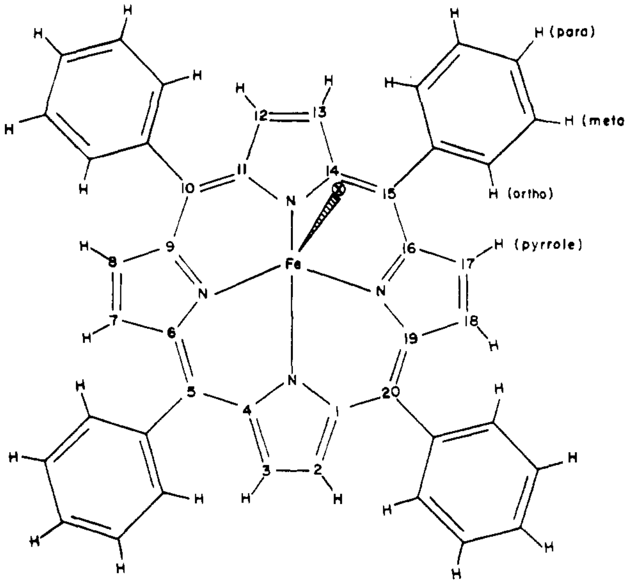

Figure 1. Molecular geometry of Fe(TPP)X.

The latter information is readily obtained from a knowledge of the contact shift. The isotropic proton shift (IPS) measured experimentally consists of the contact shift (CS) and dipolar shift (DS); the latter depends upon the magnetic anisotropy and structural parameters of the molecule.[7,8] The magnetic anisotropy term for the DS is often expressed as the anisotropy in the **g** tensor,[9] implying that this term may be zero for a high-spin ferric ion with a $^6A_1$ ground state for which *g* values are nearly isotropic. It is however now recognized that the DS contribution to the isotropic proton shift is not negligible in high-spin ferric porphyrins.[2,10,11] In fact high-spin ferric porphyrins show large anisotropy in susceptibility due to substantially large zero-field splitting of their $^6A_1$ ground electronic state. Kurland and McGarvey[12] and Bleaney[13] have therefore suggested the value of using magnetic susceptibility anisotropy data for an accurate evaluation of the DS and deduced expressions for the contact and dipolar shifts in terms of the principal susceptibility tensors for a high-spin ferric ion.

An accurate experimental determination of the DS in the high-spin ferric porphyrins has not as yet been possible because of the lack of the necessary principal magnetic susceptibility (or magnetic susceptibility anisotropy) data. Such data have however recently become available from measurements on single crystals over a temperature range of a series of high-spin ferric porphyrins, namely, (tetraphenylporphyrin)iron(III) complexes Fe(TPP)X (X = NCS, Cl, Br, I).[14-17] Availability of this data has therefore evoked interest in a detailed ^1H NMR study of this series of porphyrin molecules for the purpose of an accurate evaluation of the contact and dipolar terms, which could be a useful index in other heme systems.

Table I. Structural and Molecular Paramagnetic Anisotropy and Zero-Field Splitting (*D*) Data for the Fe(TPP)X Series

complex	Fe-N, Å	Ct-Fe, Å	Fe-X, Å	$10^6(K_\perp - K_\parallel)$,[a] cm^3/mol	*D*,[b] cm^{-1}
(TPP)Fe(NCS)	2.065	0.55	1.957	1197	5.1
(TPP)FeCl	2.060	0.39	2.192	1408	6.0
(TPP)FeBr	2.069	0.56	2.348	2934	12.5
(TPP)FeI	2.066	0.53	2.554	3168	13.5

[a] Data measured at 293 K. [b] Determined by single-crystal susceptibility measurement.

Table II. Isotropic Proton Shifts (Ppm) for the Porphyrin Compounds at 293 K

compd	pyrrole H	ortho H	ortho H'	meta H	meta H'	para H	NH
TPP	−8.85	−8.22		−7.75		−7.75	2.78
TTP	−8.85	−8.09		−7.75		−2.7[b]	2.78
(TPP)Fe(NCS)	−67.30	−0.21	2.79	−5.62	−4.42	1.20	
(TPP)FeCl	−72.40	*a*	*a*	−5.76	−4.55	1.38	
(TPP)FeBr	−73.32	−1.48	2.66	−6.72	−5.27	0.93	
(TPP)FeI	−72.30	−4.33	1.51	−7.82	−5.98	0.14	

[a] Not resolved. [b] Shift for the (*p*-CH_3) protons.

The Fe(TPP)X series has the advantage of being a very well-characterized series of high-spin iron(III) porphyrins, and detailed single-crystal structural data are available for all members of the series.[18-21] The ferric ion has a square-pyramidal geometry around it with four coordinating pyrrole nitrogen atoms pushing it slightly (~0.5 Å) out of the mean porphyrin plane toward the apical ligand (Figure 1). Some relevant structural data are listed in Table I, which immediately show the minimal structural effect on the basal porphyrin core of the variation in axial ligand. Nevertheless, electronic effects of the halides on the porphyrin, as well as in other structurally related ferric complexes, have been observed in the past.[22-24]

In the present paper we report results of our ^1H NMR studies on the Fe(TPP)X (X = NCS, Cl, Br, I) series in $CDCl_3$ over the usual range of temperature and analyze the results in the context of our discussion above.

Experimental Section

The compounds were synthesized and purified by the literature methods.[25,26] The proton magnetic resonance spectra were recorded on a 270-MHz Bruker FT NMR spectrometer in chloroform-*d* solution, the concentration of the solution being generally about 10 mM. $(CH_3)_4Si$ was used as the internal standard. The spectra were recorded in the 238–328 K temperature range with temperature being kept constant within ±1 K. The isotropic shifts for the paramagnetic complexes were corrected for the diamagnetic shift by using our experimental values of the $(TPP)H_2$.

Results and Discussion

The ^1H NMR spectra for the Fe(TPP)X series are very similar to one another; a typical spectrum for Fe(TPP)I is shown in Figure 2. The various resonances can be easily

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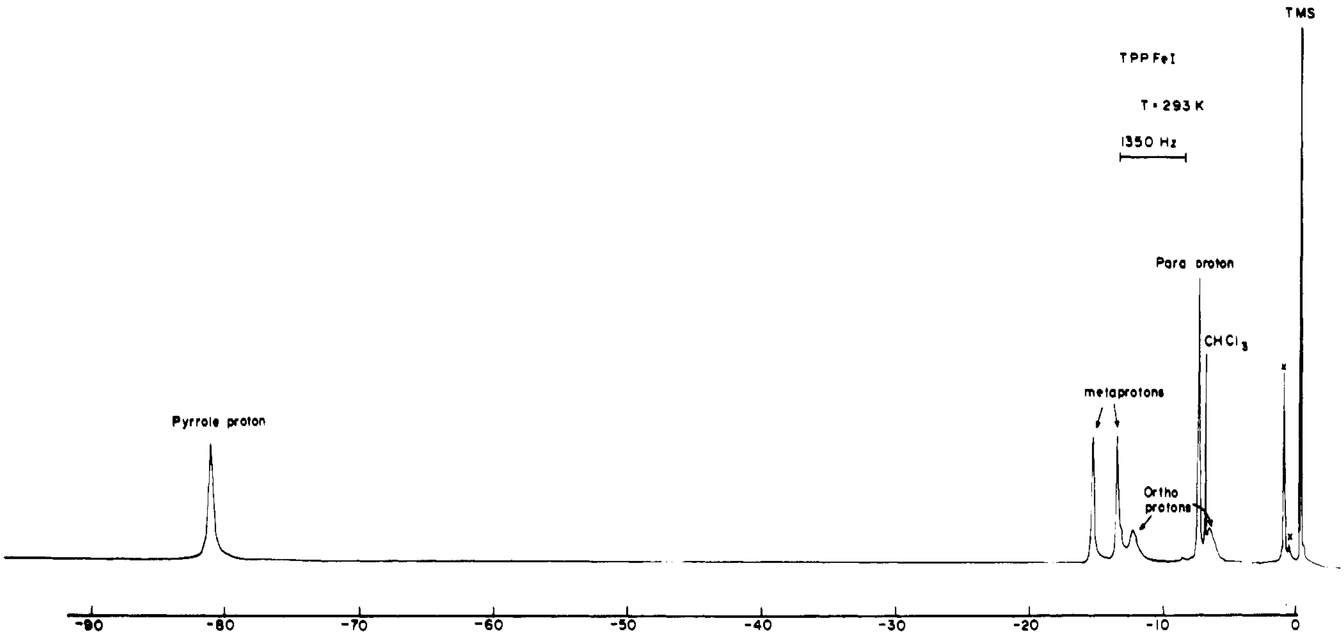

Figure 2. Proton magnetic resonance spectra of Fe(TPP)I at 293 K recorded at 270 MHz in $CDCl_3$ solution (shifts are in ppm).

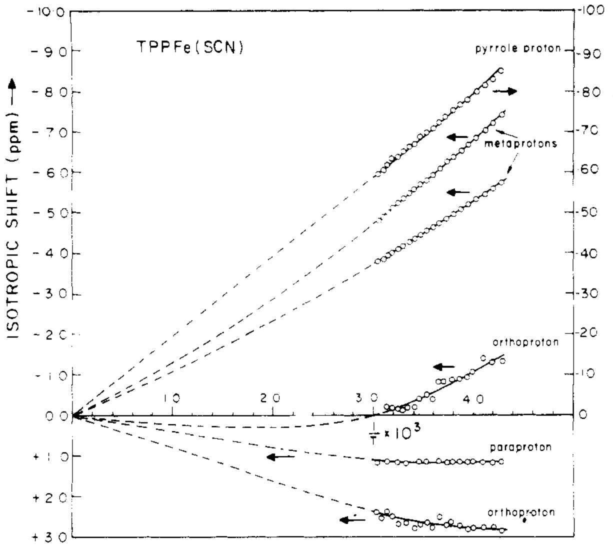

Figure 3. Temperature-dependent isotropic proton shift for (TPP)-Fe(SCN). Solid curves are calculated (see text).

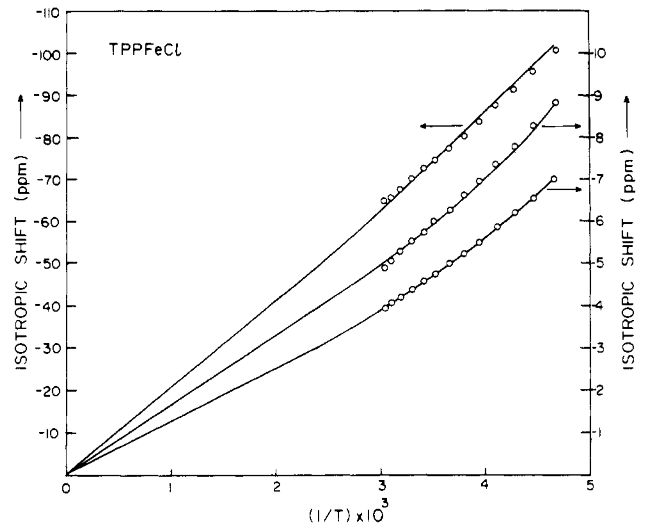

Figure 4. Temperature-dependent isotropic proton shift for (TPP)FeCl. Solid curves are calculated (see text).

assigned on the basis of the known spectrum for Fe(TTP)Cl (TTP = tetra-*p*-tolylporphyrin) and their observed characteristics.[2,10] These assignments are shown in the figure. The peaks marked X in the 1–2-ppm region are due to impurities in the sample/solvent and no attempt has been made to characterize them. The observed IPS data corrected for diamagnetism at room temperature (293 K) are given in Table II. Also included in the table are the chemical shifts for $(TPP)H_2$ and $(TTP)H_2$ measured during the present investigation. The temperature dependence of the IPS for various protons for the Fe(TPP)X series is shown in Figures 3–6.

The prominent features of the ^1H NMR spectra of the Fe(TPP)X are the large downfield shift for the pyrrole protons and the well-resolved two peaks of the phenyl meta and ortho protons. The ortho protons were not especially well resolved in all previous studies,[2,10] though for Fe(TPP)Cl they are too broad to be resolved in our study as well. The two separate peaks for these protons are observed because the iron atom, being above the mean porphyrin plane, makes the two phenyl meta and ortho protons magnetically inequivalent and because the phenyl rings are rotating in solution slowly on the NMR time scale. The rotation of the phenyl group in Fe(TTP)Cl

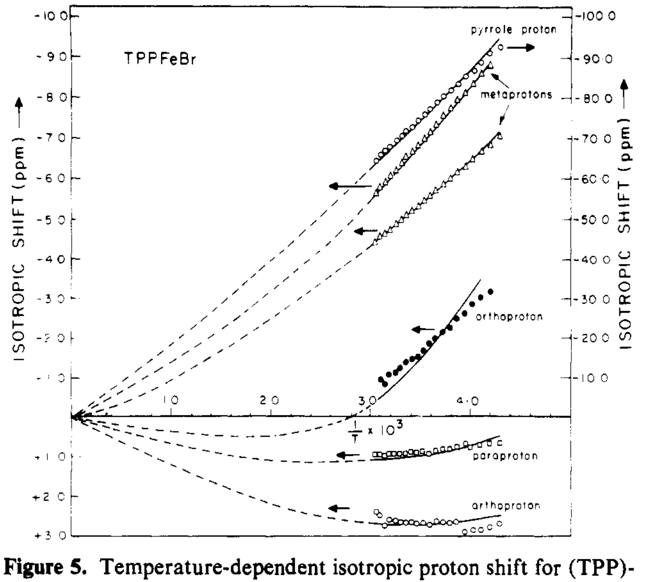

Figure 5. Temperature-dependent isotropic proton shift for (TPP)-FeBr. Solid curves are calculated (see text).

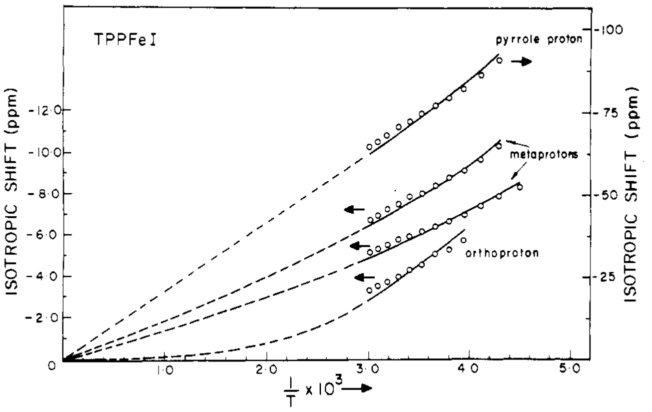

Figure 6. Temperature-dependent isotropic proton shift for (TPP)FeI. Solid curves are calculated (see text).

was studied by La Mar and Walker,[2] who osberved that the meta-proton doublets collapsed to a single line at temperatures above 60 °C. Our studies also confirm that, although the differences in the shifts between the two meta or ortho protons decrease in all the complexes with increase in temperature, they do not merge into a single line in any complex up to 58 °C, the highest temperature of our range.

The isotropic shift pattern in Table II shows some anomalies that deserve mention here. It is seen, for example, that the signs of the shifts at room temperature for the two ortho protons are different and their magnitude is smaller than that of the corresponding meta protons; the situation remains the same at lower temperatures as well. Both these observations are apparently contrary to expectations. There is no a priori reason that the two ortho protons should show shifts of opposite sign. Likewise one would have expected the shifts for the ortho protons, being closer to the metal ion, to be at least not smaller in magnitude than those for the meta protons. Further, the observed shift pattern for the series does not seem to fall into any known pattern of spin-delocalization mechanisms. These discrepancies suggest the necessity of a proper analysis of the IPS data and indicate the possibility of a substantial dipolar contribution, especially to the phenyl proton shifts.

Analysis of the Isotropic Proton Shift Data. As mentioned earlier the IPS consists of two contributions, the contact shift and the dipolar shift. McConnell and Robertson[9] had earlier derived explicit expressions for the two contributions, which indicate a $1/T$ dependence for both. The experimental data in Figures 3–6 show a substantial deviation from this behavior, especially for the phenyl protons. The general expressions deduced by Kurland and McGarvey[12] and by Bleaney[13] for the CS and DS in terms of the principal susceptibilities do, however, indicate such a deviation, as is apparent from eq 1 and 2, where (r, θ, ϕ) are the polar coordinates of the resonating proton with respect to the paramagnetic metal ion as the origin. K_i and g_i $(i = x, y, z)$ are the prinicpal susceptibilities and g tensors, A_s is the hyperfine coupling constant, and other terms have their usual meanings. It is evident that the CS and DS would follow the temperature dependence of the principal susceptibilities and anisotropies, respectively. In the case of high-spin ferric ion, simple theoretical arguments indicate a $1/T$ dependece for the principal susceptibilities and a $1/T^2$ dependence for the molecular anisotropies in the temperature region of our interest.[8] This immediately explains the deviations from the $1/T$ dependence observed in Figures 3–6 if the DS contribution is substantial.

$$(\Delta H/H)_{\mathrm{CS}} = -\frac{A_s}{3N(\gamma_N/2\pi)\beta}\left[\frac{K_x}{g_x} + \frac{K_y}{g_y} + \frac{K_z}{g_z}\right] \quad (1)$$

$$(\Delta H/H)_{\mathrm{DS}} = \frac{1}{3N}[1/2(K_x + K_y) - K_z]\left(\frac{3\cos^2\theta - 1}{r^3}\right) + \frac{1}{2N}(K_x - K_y)\left(\frac{\sin^2\theta\cos 2\phi}{r^3}\right) \quad (2)$$

Table III. Pseudocontact and Contact Shifts (Ppm) for (TPP)Fe(NCS) and (TPP)FeCl at 293 K

	(TPP)Fe(NCS)			(TPP)FeCl		
protons	$[(3\cos^2\theta - 1)/r^3] \times 10^{21}$	PCS	CS	$[(3\cos^2\theta - 1)/r^3] \times 10^{21}$	PCS	CS
pyrrole	−6.62	−4.41	−62.89	−6.35	−5.34	−67.06
ortho	−4.85	−3.21	3.00	−7.19		
ortho′	−1.81	−1.19	3.98	−1.65		
meta	−1.90	−1.25	−4.37	−1.81	−1.42	−4.34
meta′	−1.28	−0.85	−3.52	−1.39	−1.09	−3.46
para	−1.45	−0.96	2.16	−1.46	−1.14	2.52

Table IV. Pseudocontact and Contact Shifts (Ppm) for (TPP)FeBr and (TPP)FeI at 293 K

	(TPP)FeBr			(TPP)FeI		
protons	$[(3\cos^2\theta - 1)/r^3] \times 10^{21}$	PCS	CS	$[(3\cos^2\theta - 1)/r^3] \times 10^{21}$	PCS	CS
pyrrole	−6.62	−10.94	−62.38	−6.62	−11.57	−60.73
ortho	−4.85	−8.02	6.54	−4.81	−8.42	4.09
ortho′	−1.81	−2.99	5.65	−1.81		
meta	−1.90	−3.16	−3.56	−1.89	−3.30	−4.52
meta′	−1.28	−2.12	−3.15	−1.28	−2.25	−3.73
para	−1.45	−2.40	3.37	−1.44	−2.53	2.67

In axial symmetry, as in the Fe(TPP)X system, $K_x = K_y = K_\perp$ and $K_z = K_\parallel$ and hence eq 2 becomes

$$(\Delta H/H)_{\mathrm{DS}} = \frac{1}{3N}(K_\perp - K_\parallel)\left(\frac{3\cos^2\theta - 1}{r^3}\right) \quad (3)$$

The DS can be therefore accurately determined once the magnetic anisotropy $(K_\perp - K_\parallel)$ and the structural data are known, both of which are available for the present series of molecules. The experimentally determined values of $(K_\perp - K_\parallel)$ at 293 K are listed in Table I and can be used directly, with the assumption that the anisotropy of the molecule remains the same in solution. In calculating the geometric factors, especially of the phenyl protons, we note that the the phenyl rings are not static but are having a restricted rotation in solution about a mean position. This mean position need not necessarily be the same as determined by single-crystal X-ray studies. The most rigorous method of evaluating the geometric factors in solution would of course be to take an average of the values corresponding to the possible phenyl ring positions within the restricted zone of its rotation. We have however found it sufficiently accurate to calculate geometric factors by assuming that phenyl rings are perpendicular to the macroring in this mean position. The geometric factors so calculated for the various protons are listed in Tables III and IV. It is worth mentioning here that the geometric factors for Fe(TPP)Cl agree very well indeed with those calculated previously by La Mar et al.[1] With use of these values of the geometric factors and $K_\perp - K_\parallel$, the dipolar shift was calculated at 293 K and hence the CS was obtained. These are also included in Tables III and IV.

Several features of the results in Tables III and IV are worth noting. We observe that the DS is quite large for all the phenyl protons; in fact this contribution appears to be the major part in the bromo and iodo complexes. This is of course quite expected in view of their large anisotropy. The DS for the pyrrole proton is relatively much smaller; it does not exceed 14% even in the highly anisotropic iodo complex. The shift

Table V. Contact and Pseudocontact Shifts (Ppm) for (TPP)FeBr at Two Extreme Temperatures

protons	328 K CS	328 K PCS	233 K CS	233 K PCS
pyrrole	−55.10	−8.73	−77.56	−17.29
ortho	6.05	−6.40	8.51	−12.69
ortho′	5.14	−2.39	7.24	−4.74
meta	−3.10	−2.50	−4.36	−4.96
meta′	−2.74	−1.69	−3.86	−3.35
para	3.01	−1.91	4.24	−3.79

for the pyrrole protons is therefore predominantly contact in origin, in conformity with previous results.[2,10] We also observe that the CS for the phenyl protons is also significant. This is interesting since the phenyl rings are attached to the main porphyrin skeleton by a single C–C bond, and one may be tempted to assume the phenyl proton shifts to be wholly dipolar in origin.[27] Tables III and IV show that the anomalies commented upon above with respect to the IPS disappear when we compare the CS. The contact shifts for the two ortho protons now have the same sign in all the complexes, and as expected their magnitude is larger than that of the meta protons, at least in the bromo and the iodo complexes. Further, the sign of the CS for the ortho and para protons is negative and that of the meta protons positive. We shall discuss its significance below.

On the whole we observe that the dipolar contribution to the IPS in high-spin iron(III) porphyrins is quite significant at room temperature. It becomes still more important at lower temperatures, and a representative estimate for Fe(TPP)I is given in Table V. We have made use of our low-temperature single-crystal anisotropy data[17] for this purpose.

Zero-Field Splitting in Iron(III) Porphyrins. Equations 1 and 2 can be rewritten in another form by substituting expressions for K_i in terms of the zero-field splitting parameter for $S = {}^5/_2$. Such expressions can be readily deduced in axial symmetry, and their substitution gives eq 4 and 5. We have

$$(\Delta H/H)_{\mathrm{CS}} = -\frac{35 g\beta}{12(\gamma_N/2\pi)kT}\left(\frac{A_s}{h}\right) \qquad (4)$$

$$(\Delta H/H)_{\mathrm{DS}} = 289 g^2\beta^2 \frac{(3\cos^2\theta - 1)}{(3kT)^2 r^3} D \qquad (5)$$

assumed here $g_\parallel = g_\perp = 2$ for the ground ${}^6A_1$ state. Expressions 4 and 5 involve two parameters, A_s and D, and thus allow us to determine them by fitting the temperature-dependent IPS data. In practice, however, this is difficult because of the limited range of temperature over which ^{1}H NMR measurements in solution are generally done. A least-squares fit of the IPS data (Figures 3–6) to eq 4 and 5, allowing both A_s and D to vary freely, gave unacceptable values of these parameters. Similar difficulties have been encountered in the past in fitting the IPS data on Fe(TTP)Cl. We attempted therefore to fit the IPS data to only one parameter, taking either A_s or D as variable, and obtained satisfactory results. The values of the zero-field splitting parameter in this series of molecules have recently been determined accurately from single-crystal susceptibility measurements[14–17] and are listed in Table I. Using these D values, we have fitted the IPS data for all the phenyl and pyrrole protons and obtained the A_s values (Table VI). The fit is very good in all the cases (see the solid curves in Figures 3–6), and the values of A_s deduced above appear quite reasonable. This analysis lends credence to our assumption that the anisotropy of the system is the same in solution as in the solid state.

Table VI. Fermi Contact Coupling Constants, A_s (MHz), for (TPP)FeX

protons	(TPP)Fe(NCS)	(TPP)FeCl	(TPP)FeBr	(TPP)FeI
pyrrole	0.200	0.210	0.196	0.188
ortho	−0.009		−0.022	−0.014
ortho′	−0.012		−0.018	
meta	0.014	0.014	0.011	0.014
meta′	0.011	0.011	0.010	0.012
para	−0.007	−0.008	−0.011	−0.009

Table VI shows that the A_s values for the various protons in the Fe(TPP)X series are very similar and are not much affected by the iron–halogen bonding. The A_s values appear to be dominated by the iron–pyrrole nitrogen bonding, which does not show much variation in the series (see Table I). It is interesting that the ^{1}H NMR studies of structurally "related" square-pyramidal $S = {}^3/_2$ ferric bis(dithiocarbamate) halides show a linear variation in the CS with the electronegativity of the halide.[24] Absence of such a variation in the Fe(TPP)X series is in accord with the structural rigidity of the iron–porphyrin macroring as against the ferric dithiocarbamate in which changes in the axial ligand produce substantial change in Fe–S_4 bonding.[28]

Spin-Delocalization Mechanism. We finally discuss the spin-delocalization mechanism in the Fe(TPP)X series. The contact shifts resulting from the delocalization of electron spin involving σ and π orbitals have certain characteristics.[29,30] In the case of direct σ delocalization the shifts attenuate very fast and have similar sign, while rapid attenuation of the shift with alternating sign is attributed to delocalization by a spin-polarization mechanism. When spin delocalizes through ligand π molecular orbitals, the shifts alternate in sign but do not attenuate fast. The hyperfine coupling constants of the phenyl protons are of similar magnitude but alternating signs, indicating that π-type ligand molecular orbitals are involved in the spin-delocalization mechanism. This π spin transfer, which occurs mainly from the meso carbon onto the phenyl rings, is due to the fact that the phenyl rings are rotating in solution and have a finite probability of being in positions where they are not perpendicular to the porphyrin macroring.

The pyrrole protons in the Fe(TPP)X series show contact shifts that are negative and lie in the range of −60 to −70 ppm. In Fe(OEP)Cl, where the pyrrole protons are replaced by ethyl groups, the α-methylene protons show a negative contact shift, but in the range of −30 to −33 ppm.[2] This attenuation in the CS indicates that the unpaired-electron spin density of the ferric ion has delocalized through σ-type molecular orbitals to the pyrrole protons.[2]

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Registry No. (TPP)Fe(NCS), 25482-29-5; (TPP)FeCl, 16456-81-8; (TPP)FeBr, 25482-27-3; (TPP)FeI, 25482-28-4; TPP, 917-23-7; TTP, 14527-51-6.

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