1

¹H NMR spectra and electronic structure of reduced iron porphyrins: Fe(II), Fe(I) and Fe(0) porphyrins

G.N. Sinyakov*, A.M. Shulga

Institute of Physics, Belarusian Academy of Sciences, 70 F. Skoriny Prospect, Minsk 220602, Belarus

(Received 31 March 1992)

Abstract

Fe(II), Fe(I) and Fe(0) porphyrins have been generated by stepwise reduction with a sodium mirror in vacuum and their 'H NMR spectra have been recorded and analyzed. Fe(II) porphyrins (Fe(II)P) have been examined in three spin states, an S = 0 state in pyridine- d_8 , an S = 1 state in benzene- d_6 and an S = 2 state in tetrahydrofuran d_8 (THF- d_8). The analysis of isotropic shifts for low-spin Fe(II)P (S = 0) has indicated that no charge transfer has been observed. The ground state configuration is $(d_{xy})^2(d_{xz},d_{yx})^4$. The contact shifts for intermediate-spin Fe(II)P (S = 1) reflect P \rightarrow Fe π charge transfer. The proposed electron configuration is $(d_{xy})^2 (d_{z2})^2 (d_{xz}, d_{yz})^2$, which agrees with Mössbauer data. The pattern of contact shifts for high-spin Fe(II)P (S = 2) is consistent with σ spin transfer, which suggests that the $d_{x^2-y^2}$ orbital possesses an unpaired spin. The electron configuration is $(d_{xy})^2(d_{xy}, d_{yy})^2(d_{zy})^1(d_{zy})^2)^1$. Our results for Fe(II)P (S = 1, 2) agree with the literature ¹H NMR data. In the case of Fe(I)P in THF, the separation of isotropic shifts into the dipolar and contact contributions has shown the dominance of the latter. The observed shifts indicate negative π spin density on pyrrole and meso carbon atoms of the ligand, which seems to be due to a strong $\pi - \pi$ spin polarization effect. When this fact is taken into account the pattern of contact shifts is consistent with π spin transmission involving both P \rightarrow Fe π charge transfer out of the ligand-filled molecular ($3e(\pi)$) orbital and Fe \rightarrow P π^* charge transfer into the ligand highest unoccupied $(4e(\pi^*))$ molecular orbital. The occurrence of the unpaired spin in this molecular orbital is consistent with π -radical anion formulation which was found by X-ray crystallography. An S = 1/2 spin state determined by magnetic moment measurements agrees with the most probable electron configuration $(d_{xy})^2 (d_{xz}, d_{yz})^3 (d_{zz})^2$. In the case of Fe(0)P, the isotropic shifts were found to be small, providing evidence of some spin transfer. The ground state configuration is $(d_{xy})^2(d_{xz}, d_{yz})^4(d_{z2})^2$.

Introduction

The structure and redox properties of the iron porphyrins play a key role in understanding the function of hemoproteins [1]. Because hemoproteins are complex biological systems, extensive use has been made of simple synthetic porphyrin derivatives [2]. Such model compounds can be used to study electron transfer properties and the correlation between molecular structure, oxidation state and spin state. The information derived from synthetic porphyrins may be used to understand the molecular basis of structure-function relationships in hemoproteins [1-3].

Iron porphyrin complexes are found to exist in different oxidation states: Fe(III), Fe(II), and socalled Fe(I) and Fe(0) [1–3]. The studies of the electronic structure of iron porphyrins have involved

^{*} Corresponding author.

spectral [3-8], electrochemical and chemical [4,5, 9,13,20-23] determinations, magnetic moment measurements [3,10–12], Mössbauer spectra [3,11, 14,16,17,24], X-ray crystal analysis [3,11,12,14,15], resonance Raman characterization [18,19], EPR [3-5,10,15,19] and NMR [2,25-34] spectra. Many peculiarities and regularities of the properties of porphyrinatoiron(III) and porphyrinatoiron(II) complexes are known. All possible spin states have been determined. However, the electronic structure of so-called Fe(I) and Fe(0) porphyrins have never been particularly clear. These species have been obtained by reduction of Fe(II) porphyrins by one or two electrons and can be designated as $[Fe(II)P]^{-}$ and $[Fe(II)P]^{2-}$ respectively. There are many inconsistencies and ambiguities in the literature data on [Fe(II)]⁻ and Fe(II)]²⁻. The main question of whether iron or porphyrin ligand reduction has occurred in these species has had no clear answer until now.

The proton NMR method, as a powerful tool for investigating molecular structure, can provide new information about the nature of Fe(I) and Fe(0) porphyrins. If iron porphyrin complexes in different oxidation and spin states are paramagnetic ions, considerable information on the π bonding, ground state orbital configuration and structure-function relationship can be derived from the chemical shifts [2]. Fe(III) porphyrins in all possible spin states have been studied by proton NMR [2,30,31,34]. The ¹H NMR spectra of high-spin (S = 2) and intermediate-spin (S = 1) ferrous porphyrin complexes have also been reported [2,32,33].

To aid in obtaining new information about the electronic structure of Fe(I) and Fe(0) porphyrins we have studied their ¹H NMR spectra. We have also examined the ¹H NMR spectra of ferrous porphyrins in different spin states (S = 0,1,2). Fe(II) porphyrins in high-spin state, which have been investigated by Goff and La Mar [33] were complexes of synthetic porphyrins with a 2-methylimidazole ligand [Fe(II)P(2-MeIm)]. Fe(II) porphyrins in an S = 1 spin state were prepared in benzene by reaction with aqeuous dithionite or the chromous reduction [32].



Fig. 1. Structural formulae of iron porphyrins.

We prepared Fe(II), Fe(I) and Fe(0) porphyrins by reduction of Fe(III) porphyrin chloride with sodium (see below). The ¹H NMR spectra in an S = 1 spin state in benzene- d_6 agrees with the data of ref. 32. The chemical shifts of high-spin S = 2ferrous porphyrins in tetrahydrofuran [Fe(II)-P(THF)] differ from the chemical shifts of [Fe(II)P(2-MeIm)] [33]. The ¹H NMR spectra of the ferrous porphyrins under study in an S = 0 spin state and Fe(I) and Fe(0) porphyrins are absent in the literature.

The synthetic porphyrins selected for our study are complexes of 2,3,7,8,12,13,17,18-octaethylporphyrinato-Fe(III)Cl (FeOEP), 5,10,15,20-tetrapropylporphyrinato-Fe(III)Cl (FeTPrP), 5,10,15,20tetraphenylporphyrinato-Fe(III)Cl (FeTPhP) and 2,8,12,18-tetramethyl-13,17-diethyl-5-phenylporphyrinato-Fe(III)Cl (FePhTMDEP). The structural formulae are presented in Fig. 1. The aims of the porphyrin choice will be discussed later.

Experimental

OEP [35], TPhP [36], TPrP [37] and PhTMDEP [38] were prepared by methods described in the literature. Iron insertion was performed in a dimethylformamide reflux with use of excess FeCl₃ [39]. The product was precipitated by dilute HCl solution.

Fe(II), Fe(I) and Fe(0) porphyrins were obtained in THF- d_8 solution by means of contact with a sodium mirror in the reaction vessel. The optical cell and NMR tube were sealed to the reaction vessel. A piece of sodium metal and Fe(III) porphyrin chloride (4-6 mg) were introduced into different parts of the reaction vessel. The latter was evacuated to below 10^{-4} mm Hg and then a film of pure sodium was obtained by sublimation. About 10-15 ml of solvent was distilled from a storage bulb containing THF-d₈ and Na-K alloy. When the porphyrin had dissolved in the THF solution, it was poured into the part of the reaction cuvette with the sodium mirror and the reaction was allowed to take place. Successive additions of one, two or three electrons to Fe(III) porphyrin chloride result in Fe(II), Fe(I) or Fe(0) porphyrin respectively. The electronic absorption spectra were examined during the reduction reaction. Contact of the solution with sodium was stopped as soon as the Fe(III) porphyrin chloride was completely transformed into Fe(II), Fe(I) or Fe(0) porphyrins. The procedure of the porphyrin stepwise reduction has been described in detail elsewhere [40,41].

The solutions of ferrous porphyrins in benzene d_6 and pyridine- d_5 were prepared by the following procedure. When Fe(II)P was produced in THF the solvent was distilled back from the reaction vessel and the latter was evacuated for two hours until the residual pressure reached 10⁻⁴ mm Hg with simultaneous heating to 60°C. Then the required quantity of benzene- d_6 or pyridine- d_5 was distilled into the reaction cuvette from the storage bulb. When the ferrous porphyrin residue was dissolved the solvent was poured into the NMR tube and the latter was sealed off. THF- d_8 and benzene- d_6 were purified by contact with Na-K alloy for several days in vacuo. Pyridine- d_5 was not purified; it was degassed by successive freeze-thaw pumping cycles only. In the cases of THF- d_8 and pyridine- d_5 solution, the concentration of iron porphyrins in the NMR tube was $(1-2) \times 10^{-2}$ M. The concentration of Fe(II)P in benzene- d_6 solution was less than 5-10 times that of the THF and pyridine solutions because of the low solubility of the ferrous porphyrin residue in benzene- d_6 .

Electronic absorption spectra were recorded using Beckman UV 5270 and SF-10 spectrophotometers. A Bruker WM-360 NMR instrument with an operating frequency of 360.13 MHz was used to obtain the proton NMR spectra. The chemical shifts were referred to TMS as internal standard.

Results and discussion

Electronic absorption spectra

Stepwise reduction of iron porphyrins results in a change in the electronic absorption spectra as described in the literature for FeOEP [8,19] and FeTPhP [3–5]. The absorption spectra of Fe(II), Fe(I) and Fe(0)OEP which were measured by us correspond to published data [8,19]. We have observed apparent inconsistencies in optical specification of Fe(0)TPhP [3] and we will discuss this in detail later. The optical spectra of FeTPrP and FePhTMDEP are absent in the literature. We represent these spectra in Figs. 2 and 3.

The first step in the interaction between a solution of Fe(III)PCl and Na is the production of Fe(II)P by means of the reaction Fe(III)PCl + Na \rightarrow Fe(II)P + NaCl. The spectrum of Fe(II)TPrP is shown by curve 1 in Fig. 1. These reduced species have a spectrum typical of ferrous porphyrins: a high-intensity Soret band, two bands of approximately equal intensities in the region 520-580 nm, and low-intensity bands in the far-infrared. Maxima at 615 nm are absent in the spectra of Fe(II)OEP and Fe(II)PhTMDEP. For Fe(II)TPhP the observed spectrum is 426 Soret, 540, 555 sh, 600 sh, and 820 sh nm (broad, low intensity) in agreement with refs. 3-5.

The formation of Fe(I) porphyrins is accompanied by further spectral changes. The spectrum of Fe(I)TPrP has the Soret band split into three components at 330, 400 and 430 nm, and three bands at 625, 705 and 730 nm (curve 2 in Fig. 2). In the case of Fe(I)TPhP, the spectrum is close to that



Fig. 3. Absorption spectra of: (1) Fe(II)TPrP in pyridine- d_5 and (2) benzene- d_6 ; (3) Fe(II)PhTMDEP in pyridine- d_5 ; and (4) benzene- d_6 .

of Fe(I)TPrP (Soret band at 330, 392 and 425 nm, a band at 513 nm and broad weak bands at 578, 672 and 715 nm). The observed spectrum of Fe(I)TPhP resembles that of the so-called B form of Fe(I)TPhP obtained by electrochemical reduction in dimethyl-formamide.^a

Curve 3 in Fig. 2 shows the spectrum of Fe(0)TPrP. The Soret band is split into two components at 363 and 460 nm, two bands are observed at 520 and 545 sh nm, and two weak bands appear in the far-infrared at 705 and 800 nm. In the spectrum of Fe(0)TPhP the corresponding bands are observed at 355 and 428 nm (Soret), at 516 nm, and at 715 and 775 nm (weak bands). The maxima of the intense bands agree with those of Lexa et al. [4], although the authors have not reported the absorbance curve and the weak bands. The spectrum over the range 350–600 nm is also similar to that of form A obtained by electrochemical reduction [5]. However, there are discrepancies in



Fig. 2. Absorption spectra of (1) Fe(II)TPrP, (2) Fe(I)TPrP and (3) Fe(0)TPrP in THF- d_8 solution.

the Fe(0)TPhP spectrum as described by Reed in his review [3]. It seems that the spectrum which Reed has attributed to Fe(0)TPhP corresponds to more highly reduced species. It was pointed out that the solution of Fe(0)TPhP was green. We found that the colour of Fe(0) porphyrin solutions looked yellow for Fe(0)TPhP, orange for both Fe(0)TPrP and Fe(0)PhTMDEP, and brown for Fe(0)OEP. The brown colour of the Fe(0)OEPsolution was also noted in ref. 19. During prolonged contact of the studied Fe(0) porphyrins with sodium we have observed that two reduction stages occur. The chemical species which correspond to the first stage looked green. Their spectra are close to that reported by Reed [3]. These highly reduced iron porphyrins proved to be unstable species. During this time, bands of the Fe(I) porphyrins appear in the spectra and new bands are observed which we cannot yet assign to a chemical species. The possibility of iron porphyrin reduction below Fe(0) porphyrins is pointed out in refs. 4, 8 and 19.

Fe(I) and Fe(0) porphyrins in benzene and pyridine solutions are also unstable species. The spectra of Fe(II)TPrP and Fe(II)PhTMDEP in benzene and pyridine solution are present in Fig. 3.

¹H NMR is very sensitive to the presence of other reduction products in the solution under study

^aIt should be noted that during the controlled potential electrolysis the appearance of two species (A and B forms) was observed in succession both for Fe(I) and Fe(0) porphyrins [4,5]. Under the chemical reduction with sodium, a detailed analysis of the spectra has shown the appearance of only one product, as for Fe(I) and Fe(0) porphyrins (see later). This agrees with data in ref. 19.

Table 1

Proton chemical shifts (ppm, referred to internal TMS) of ferrous porphyrins in THF- d_8 (S = 2), benzene- d_6 (S = 1) and pyridine- d_5 (S = 0)

| Compound | Solvent | Chemical shifts | | | | | |
|-----------|----------|-------------------------------|-------------------|-------------------|--------------------------|-------------|--|
| | | Pyrrole | | Meso | | | |
| FeOEP | | α-CH ₂ | β-CH ₃ | н | | <u> </u> | |
| | THF | 12.50 | 2.54 | 18.87 | | | |
| | Benzene | 34.00 | 13.00 | 76.30 | | | |
| | Pyridine | 4.02 | 1.95 | 10.04 | | | |
| FeTPrP | | Н | | α-CH ₂ | β -CH ₂ | γ-CH | |
| | THF | 48.92 | | - 3.79 | 0.47 | 0.16 | |
| | Benzene | 6.06 | | 16.65 | 14.73 | 6.94 | |
| | Pyridine | 9.51 | | 4.72 | 2.40 | 0.83 | |
| FeTPhP | | Н | | <i>o-</i> H | <i>m</i> -H | <i>p</i> -H | |
| | THF | 49.74 | | 6.52 | 6.27 | 6.88 | |
| | Benzene | 6.29 | | 20.19 | 12.10 | 12.32 | |
| | Pyridine | 8.92 | | 8.22 | 7.67 | 7.67 | |
| FePhTMDEP | | Н | | 15-H | 10,20-H | | |
| | THF | 51.31 | | 16.86 | 13.35 | | |
| | | α -CH ₂ | β-CH ₃ | <i>o</i> -H | <i>m</i> -H | <i>р</i> -Н | |
| | | 8.01 | 1.35 | 7.31 | 6.52 | 7.28 | |
| | | 2,8,12,18-CH ₃ | | | | | |
| | | 10.10, 10.10 | | | | | |
| | Benzene | | | 15-H | 10,20-H | | |
| | | Not observed | | 68.77 | 81.20 | | |
| | | α -CH ₂ | β-CH ₃ | <i>o</i> -H | m-H | <i>р</i> -Н | |
| | | 30.57 | 11.39 | 19.34 | 12.13 | 12.49 | |
| | | 2,8,12,18-CH, 51.78, 48.11 | | | | | |

because of the broadening effects. Hence, after careful analysis of the absorption spectra of all the reduced iron porphyrins, the process of reduction was controlled by the appearance of new species bands and the disappearance of bands of past products.

Proton NMR spectra

The chemical shifts of ferrous porphyrins in S = 0, 1 and 2 spin states are listed in Table 1. The NMR spectra are illustrated in Fig. 4 for Fc(II)TPhP, as an example. In the case of Fe(II)P in pyridine- d_6 solution, the chemical shifts cover the range 0-10 ppm, typical for the complexes of por-

phyrins with diamagnetic metals. The spectra were run with 16 K data points over 6024 Hz, giving a digital resolution of 0.75 Hz. The signals are wellresolved and the assignments do not present any difficulties.

The chemical shifts of Fe(II)P in THF and benzene solutions cover the range up to 76 ppm. The spectral width used provides an accuracy of 0.01 ppm. As a rule the proton signals are broadened in these solutions. However, when double resonance was used, the change of multiplicity enabled us to assign the signals to corresponding substituent protons.

The chemical shifts of Fe(I) and Fe(0) porphyrins in THF- d_8 solution are presented in Table



Fig. 4. ¹H NMR spectra of Fe(II)TPhP in (a) THF- d_8 , (b) benzene- d_6 and (c) pyridine- d_5 solution. *, solvent signals.

2. The proton traces of Fe(I)P are observed from -18.40 to 55.43 ppm. An example of the Fe(I)P spectrum is shown for Fe(I)PhTMDEP in Fig. 5. Fe(I)P spectra exhibit signals which are as broad as 300 Hz for the protons attached to the porphyrin macrocycle (meso-H, pyrrole-H, α -CH₂). However, the resolution of the Fe(0)P spectra is close to that of diamagnetic metalloporphyrins (Fig. 6). The chemical shifts of Fe(0) porphyrins also cover the range typical for diamagnetic metalloporphyrins.

Analysis of the chemical shifts

In the analysis of the chemical shifts of paramagnetic molecules, attention is focused on the effects of the unpaired electron on the resonance signal of the nucleus. Hence, we consider only the difference between the chemical shifts of the paramagnetic compound and those of the suitable diamagnetic molecule. In the case of the iron porphyrins, the corresponding diamagnetic nickel(II) complexes are usually used. The obtained difference is the isotropic shift $(\Delta H/H)^{iso}$ which is the sum of two interactions, those of the dipolar $(\Delta H/H)^{dip}$ and the contact $(\Delta H/H)^{con}$. The dipolar contribution arises from interaction of the net magnetic moment of the unpaired electron with the nuclear spin via a through-space dipolar mechanism. For effective axial symmetry the dipolar shift is given [42] by

$$(\Delta H/H)^{dip} = -\frac{\beta^2 S(S+1)}{9kT} (g_{\parallel}^2 - g_{\perp}^2) \times (3\cos^2\theta - 1)/r^3$$
(1)

where θ is the angle between the nucleus-metal vector and the z axis, r is the length of this vector, and g_{\parallel} and g_{\perp} are the EPR g values. This oversimplified equation neglects the second-order Zeeman interaction.

The contact interaction arises from spin transfer between the paramagnetic atom and the ligand and thus provides information on the metal-ligand bonding. The simplified equation [42] is

$$\left(\frac{\Delta H}{H}\right)^{\rm con} = -A \frac{g\beta S(S+1)}{3\gamma_{\rm N}hkT}$$
(2)

where A is the Fermi contact coupling constant which reflects the size and sign of the transferred spin density. Hence, under certain conditions, valuable information about the nature of the ligand molecular orbital (MO) can be provided from the contact shifts. The contact shifts which are of prime interest are obtained by subtracting the estimated (or calculated) dipolar shifts from the observed isotropic shifts. The dipolar shifts can be calculated using Eq. (1) if g_{\parallel} and g_{\perp} are known. In the absence of magnetic anisotropy data, the dipolar contribution can be estimated by the observed temperature dependence of the shifts.

When the contact shifts of iron porphyrins are available, attention is focused on the shifts of an attached proton and methyl (or methylene) groups Table 2

| Compound | Iron | Chemical shifts | | | | | | |
|-----------|--------------------|-------------------------------------|-------------------|-------------------|-------------------|--|--|--|
| | oxidation state | Pyrrole | | Meso | | | | |
| FeOEP | | α-CH, | β-CH ₃ | Н | | To the second seco | | |
| | Ι | - 2.30 | 1.98 | 55.43 | | | | |
| | 0 | 3.32 | 1.98 | 14.83 | | | | |
| FeTPrP | | Н | | α-CH ₂ | β-CH ₂ | γ-CH ₃ | | |
| | Ι | 27.31 | | -18.40 | 4.60 | 1.48 | | |
| | 0 | 12.02 | | 2.96 | 2.92 | 1.49 | | |
| FeTPhP | | Н | | <i>o</i> -H | <i>m</i> -H | <i>p</i> -H | | |
| | Ι | 29.46 | | 14.30 | 7.10 | 9.55 | | |
| | 0 | 11.73 | | 8.95 | 7.61 | 7.76 | | |
| FePhTMDEP | | Н | 15-H | 10,20-H | | | | |
| | I | 27.56 | 59.50 | 49.00 | | | | |
| | 0 | 10.95 | 14.67 | 15.08 | | | | |
| | | α -CH ₂ | β-CH ₃ | o-H | <i>m</i> -H | <i>p</i> -H | | |
| | Ι | -1.62 | 3.02 | 14.27 | 6.90 | 9.53 | | |
| | 0 | 3.50 | 1.98 | 8.70 | 7.62 | 7.75 | | |
| | I | 2,8,12,18-CH ₃ - 4.77 | | | | | | |
| | | 12.18-CH | 2.8-CH | | | | | |
| | 0 | 2.13 | 2.09 | | | | | |

Proton chemical shifts (ppm, referred to internal TMS) of Fe(I) and Fe(0) porphyrins in THF-d₈

at the pyrrole and meso positions. It has been shown [2] that in the case of spin transfer to the ligand σ MO, the proton and methylene shifts, being larger for the former than the latter, are the same sign (downfield). For spin transfer to the porphyrin π MO, the contact shifts are characterized by upfield proton and downfield methylene shifts which are of comparable magnitude. When such contact shifts are observed at the meso position, the spin transfer occurs through por-



Fig. 5. Proton NMR spectrum of Fe(I)PhTMDEP in THFd₈ solution. *, solvent signals.



Fig. 6. Proton NMR spectrum of Fe(0)PhTMDEP in THFd₈ solution. Solvent signals are omitted for clarity.

phyrin \rightarrow metal (P \rightarrow M) π charge transfer. The same shifts at the pyrrole position result from M \rightarrow P π^* charge transfer.

Thus, if we want to provide information about metal-ligand bonding we must have at our disposal a series of iron porphyrins with proton and methyl (or methylene) groups at both the meso and pyrrole positions. The selected synthetic porphyrins provide the necessary probes for the pyrrole and meso spin density. It should be noted that the FePhTMDEP complex is a suitable compound because the unsubstituted 3,7 positions, and the 2,8,12,18-methyl and 13,17-ethyl substituents provide the necessary probes for the spin density at the pyrrole positions. In addition, using FePhTMDEP (and FeTPhP) provides a means for the determination of the dipolar shifts. It has been shown [2,30-34] that the phenyl protons are not involved in spin transmission, and isotropic shifts for these positions may be assumed to be wholly dipolar in origin. According to Eq. (1) the dipolar shifts are proportional to the relative geometric factors $(3\cos^2\theta - 1)/r^3$. Hence, if the dipolar shifts for the phenyl protons are determined and the geometric factors for all their positions are known, it is possible to calculate the dipolar contribution for all the remaining positions. The relative geometric factors have been computed for all the porphyrin positions using available X-ray data [2,30-34].

We were encouraged in our analysis of isotropic shifts by similar investigations of Fe(III) and Fe(II) porphyrins reported by La Mar and co-workers [2,30-34]. We shall compare our results on the ferrous porphyrins in an S = 1,2 spin state with their data later. To avoid confusion it should be noted that we use the recommended δ -scale which increases in a downfield direction relative to TMS, but La Mar and co-workers have used a δ -scale which increases in the opposite direction. In order to compare the sign of the isotropic shifts observed by La Mar and by us, we have to calculate $\delta_{iso} = \delta_{Ni} - \delta_{Fe}$ instead of $\delta_{iso} = \delta_{Fe} - \delta_{Ni}$.

The chemical shifts of diamagnetic Ni(II) porphyrins have been measured in CDCl₃ solutions relative to internal TMS. NiOEP: 9.79 (s, H-5, 10, 15,20), 3.93(q) and 1.82 (t, CH_3CH_2 -2,3,7,8, 12,13, 17,18). NiTPrP: 9.24 (s, H-2,3,7,8,12,13, 17,18) 4.46(t), 2.23 (sextet) and 1.10 (t, 5,10,15,20-CH₂-CH₂-CH₃). NiPhTMDEP: 9.78 (s, H-10,20), 9.73 (s, H-15), 8.53 (q, H-3,7) 8.01 (m, *o*-H, 5-Ph), 7.70 (m, *m*, *p*-H-5-Ph), 3.48 (d, CH₃-2,8), 3.47 (s, CH₃-12,18), 3.91(q) and 1.78 (t, CH₃CH₂-13,17). The chemical shifts of NiTPhP are taken from ref. 43.

Iron(II) porphyrins

An S = l spin state

Intermediate-spin Fe(II) porphyrins in benzene d_6 are four-coordinate unligated complexes. The isotropic shifts of Fe(II)P are listed in Table 2. The observed shifts of ferrous porphyrins are similar to those described by La Mar and co-workers [2,32]. All isotropic shifts are downfield except for pyrrole-H shifts. This behavior of the shifts enables us to conclude that the contribution of dipolar interaction to isotropic shifts is rather large.

The shifts of most of the phenyl protons were found to originate in the dipolar interaction. Utilizing calculated geometric factors, La Mar et al. [32] have obtained the dipolar contribution for all the remaining positions. Subtracting the dipolar from the isotropic shifts we obtained the contact shifts which are presented in Table 2.

Analysis of the contact shifts shows that upfield proton and downfield α -CH₂ contact shifts are observed at the pyrrole position. The shifts have comparable magnitudes. This indicates that a significant amount of positive π spin density is placed on the pyrrole carbon atoms. Since the highest filled MO, $3e(\pi)$, exhibits a large positive π charge density on the pyrrole carbon atoms, but possesses nodes through the meso carbons, the contact shifts at the pyrrole positions indicate spin transmission involving P \rightarrow Fe π charge transfer out of the $3e(\pi)$ MO. The downfield proton and upfield α -CH₂ contact shifts at the meso position suggest a negative spin density on the meso carbons due to correlation effects. P \rightarrow Fe π charge transfer was

| Substituent position | S = 1 (benze | $ne-d_6)$ | . <u>.</u> , | S = 2 (THF) | | | |
|-------------------------------------|--------------|-----------|--------------|--------------|----------------------|---------|--|
| (ligand) | Isotropic | Dipolar | Contact | Isotropic | Dipolar ^b | Contact | |
| Pyrrole | | | | | | | |
| H(TPrP) | 3.18 | -21.80 | 24.98 | - 39.68 | 3.10 | - 42.78 | |
| H(TPhP) | 2.51 | -21.80 | 24.31 | -41.00 | 3.10 | - 44.10 | |
| H(PhTMDEP) | | | | -42.78 | 3.10 | - 45.88 | |
| α -CH ₂ (OEP) | - 30.10 | -13.20 | - 16.90 | -8.57 | 1.90 | - 10.47 | |
| α -CH ₂ (PhTMDEP) | -26.60 | -13.20 | -13.40 | -4.10 | 1.90 | - 6.00 | |
| Meso | | | | | | | |
| H(OEP) | - 66.54 | - 34.10 | - 32.44 | -9.11 | 4.90 | - 14.01 | |
| 15-H(PhTMDEP) | - 59.04 | -43.10 | - 29.44 | - 7.13 | 4.90 | - 12.03 | |
| 10,20-H(PhTMDEP) | - 71.42 | - 34.10 | -37.32 | -3.57 | 4.90 | - 8.47 | |
| α -CH ₂ (TPrP) | -12.19 | -18.70 | 6.51 | 13.03 | 2.72 | 10.31 | |
| o-H(TPhP) | - 12.39 | -11.20 | - 1.19 | 1.28 | 1.60 | -0.32 | |
| o-H(PhTMDEP) | -11.13 | -11.20 | 0 | 0.70 | 1.60 | - 0.32 | |
| <i>m</i> -H(TPhP) | - 4.43 | - 5.00 | 0.40 | 1.23 | 0.80 | 0.43 | |
| <i>m</i> -H(PhTMDEP) | - 4.43 | -5.00 | 0 | 1.18 | 0.80 | 0.38 | |
| <i>p</i> -H(TPhP) | -4.82 | - 4.70 | -0.12 | 0.82 | 0.70 | 0.12 | |
| <i>p</i> -H(PhTMDEP) | - 4.79 | 4.70 | 0 | 0.42 | 0.70 | - 0.28 | |

Separation of isotropic shifts of Fe(II) porphyrins in an S = 1 and S = 2 spin state into dipolar and contact contributions (ppm)

Table 3

^bRef. 33.

found to require that the (d_{xz}, d_{yz}) orbitals have unpaired spin. This type of spin transfer occurs in low-spin Fe(III) and high-spin Mn(III) porphyrins [2,31,44]. The pattern of contact shifts provides no evidence for σ spin transfer. This indicates that the $d_{x^2-y^2}$ orbital is vacant. Taking into account the dominance of $P \rightarrow Fe \pi$ charge transfer, and the Mössbauer data [11] and measurements of the magnetic moment [11], a reasonable configuration of the intermediate-spin Fe(II) porphyrins is $(d_{xy})^2(d_{z2})^2(d_{xz}, d_{yz})^2$.

An S = 2 spin state

It is known that Fe(II) porphyrins in THF coordinate only one molecule of solvent [7,9,19]. These five-cordinate complexes exist in the high-spin state. The complexes of Fe(II) porphyrins with 2-methylimidazole are also high-spin. The isotropic shifts of Fe(II)P(THF) (Table 3) are close to those of Fe(II)P(2-MeIm) for the pyrrole positions [33]. The phenyl proton shifts are also comparable. However, a discrepancy is observed for the meso position. The downfield proton shift (-9.11 ppm) measured by us differs strongly from the value (+7.0 ppm) obtained by La Mar, Walker and Goff [2,33]. These authors have calculated the dipolar shifts which we have used to determine the contact shifts of Fe(II)P(THF)^a; the latter are listed in Table 3.

The results show that the contribution of contact shifts dominates the isotropic effect. Both the downfield proton and α -CH₂ contact shifts, the former having a large value, occur at the pyrrole position. The downfield proton and upfield methylene contact shifts, having comparable magnitudes, are observed at the meso position. The pattern of contact shifts indicates σ spin transfer at the pyrrole position and the occurence of a negative spin

^aRef. 32.

^aThe dipolar shifts of meso α -CH₂ have been calculated by us from the data in ref. 32.

density on the meso carbons due to correlation effects.

In the case of Fe(II)OEP(2-MeIm), [2,33] the relatively small upfield meso H contact shifts suggest a moderate positive π spin density at the meso position.^a The discrepancy in the shifts at the meso position for Fe(II)OEP(2-MeIm) and Fe(II)-OEP(THF), both high-spin, appears to account for the difference in the intramolecular interactions in these complexes. The electrons of iron are bonded more strongly to 2-MeIm than to THF, which is reflected by the pattern of spin delocalization at the meso positions. It should be noted that for Fe(II) porphyrin complexes with two THF molecules, the data derived from low-temperature (100 K) X-ray diffraction analysis [45] provide evidence for σ donation from the porphyrin ligands to the iron atom and significant Fe \rightarrow P π charge transfer to $4e(\pi^*)$ MO (back-bonding).

Let us focus our attention on the electron configuration. Large amounts of σ delocalization to the pyrrole position for both high-spin Fe(II)P(2-MeIm) and Fe(II)P(THF) indicates that the $d_{x^2-y^2}$ orbital exhibits a lone spin. The same σ spin transfer was found for high-spin Fe(III)P [2], providing evidence for an unpaired electron in the $d_{x^2-y^2}$ orbital. Thus, the electron configuration of the high-spin Fe(II) porphyrins is probably $(d_{xy})^2$ $(d_{xz}, d_{yz})^2 (d_{z2})^1 (d_{x^2-y^2})^1$. But, as La Mar and Walker have noted [2], it is also conceivable that the electron configuration could be $(d_{xz}, d_{yz})^3 (d_{xy})^1$ $(d_{z^2})^2 (d_{x^2-y^2})^1$.

An S = 0 spin state

Ferrous porphyrins in pyridine solution are sixcoordinate complexes Fe(II)P(Py₂). The isotropic shifts are given in Table 4. All shifts are downfield. However, the very small magnitudes of the shifts provide no evidence for the pronounced charge transfer. The ground state is $(d_{xy})^2(d_{xz},d_{yz})^4$.

Table 4

Isotropic shifts of Fe(II) porphyrins (ppm, internal TMS) in an S = 0 spin state in pyridine-d, solution

| Substituent position (ligand) | Shift | |
|----------------------------------|--------|--|
| Pyrrole | | |
| H(TPrP) | -0.27 | |
| H(TPhP) | -0.10 | |
| α -CH ₂ (OEP) | - 0.09 | |
| Meso | | |
| H(OEP) | -0.28 | |
| α -CH ₂ (TPrP) | -0.26 | |
| o-H(TPhP) | -0.42 | |
| m-H(TPhP) | -0.17 | |
| p-H(TPhP) | -0.17 | |

Iron(I) porphyrins

The isotropic shifts of Fe(I) porphyrins are presented in Table 5. The pattern of the isotropic shifts suggests that a major portion of the shifts originate in the contact interaction. For separation of the isotropic shifts we have calculated the

Table 5

Separation of isotropic shifts of Fe(I) porphyrins in THF- d_8 into dipolar and contact contributions

| Substituent position (ligand) | Isotropic shift | Geometric factor ^a | Dipolar shift | Contact shift |
|-------------------------------------|--------------------|----------------------------------|------------------|------------------|
| Pyrrole | | | | |
| H(TPrP) | -18.07 | -7.03 | - 5.69 | -12.38 |
| H(TPhP) | - 20.70 | -7.03 | - 5.69 | -15.01 |
| H(PhTMDEP) | - 19.03 | -7.03 | - 5.69 | -13.34 |
| α -CH ₂ (OEP) | +6.23 | -4.25 | - 4.89 | +11.12 |
| α -CH ₂ (PhTMDEP) | + 5.53 | -4.25 | - 4.89 | + 10.42 |
| Meso | | | | |
| H(OEP) | -45.67 | - 11.00 | - 8.91 | - 36.76 |
| 15-H(PhTMDEP) | - 49.77 | -11.00 | - 8.91 | - 40.86 |
| 10,20-H(PhTMDEP) | - 39.22 | -11.00 | - 8.91 | - 30.31 |
| α -CH ₂ (TPrP) | + 22.86 | -6.04 | -4.89 | +27.75 |
| o-H(TPhP) | -2.05 | - 3.61 | -2.93 | +0.88 |
| o-H(PhTMDEP) | -6.26 | - 3.61 | -2.93 | - 3.33 |
| m-H(TPhP) | -6.50 | -1.67 | -1.35 | - 5.15 |
| m-H(PhTMDEP) | +0.80 | - 1.67 | -1.35 | +2.15 |
| p-H(TPhP) | +0.40 | -1.48 | -1.20 | +1.60 |
| <i>p</i> -H(PhTMDEP) | - 1.83 | - 1.48 | -1.20 | - 0.63 |

^aGeometric factor $(3\cos^2\theta - 1)r^{-3}10^{21}$ cm⁻³ is taken from ref. 32.

^aThe meso α -CH₂ contact shifts have not been presented in refs. 2 and 33.

dipolar contribution using Eq. (2). The relative geometric factors was taken from ref. 2. The values of g_{\parallel} and g_{\perp} have been measured by many authors [3,4,10,15,19]; we have used the values $g_{\perp} = 2.26$ and $g_{\parallel} = 1.93$ [19]. The calculated dipolar and contact shifts are also given in Table 5.

As mentioned above, the shifts of the phenyl protons can be used to test the dipolar contribution. Indeed, the dipolar shifts prevail at the ortho position for Fe(II)TPhP and the para position for Fe(II)PhTMDEP. However, the contact shifts at the remaining positions of the phenyl ring suggest an appreciable contact contribution to the isotropic shifts. Shift direction alternates around the phenyl ring, also indicating an appreciable contact contribution. Analysis of the pyrrole and meso contact shifts indicates the apparent dominant contact contribution at these positions. Large downfield meso H shifts and upfield meso α -CH₂ shifts of comparable magnitude are evidence for the pronounced negative π spin density on the meso carbons. The same shifts, although smaller in magnitude at the pyrrole position, indicate a negative π spin density on the pyrrole carbons as well. This pattern of a sizable negative π spin density at both the pyrrole and meso positions has not been observed before. The negative sign of the spin density cannot be used as an argument against spin transmission. If the sign was positive the spin transfer mechanism would involve $P \rightarrow Fe \pi$ charge transfer at the pyrrole positions and $Fe \rightarrow P \pi^*$ charge transfer at the meso positions. We believe that the former and the latter both actually take place. The negative sign of the π spin density should not cause confusion; it may be due to a strong π - π spin polarization effect. It should be noted that many organic π -anion radicals exhibit a negative π spin density, for example those of pyrene [46,47]. The occurrence of a negative π spin density follows logically from quantum-chemical MO calculations [47].^a

Thus, if we pay no attention to the negative sign of spin delocalization, the pattern of spin transfer is consistent with $P \rightarrow Fe \pi$ charge transfer from the highest filled ligand MO ($3e(\pi)$) and $Fe \rightarrow P \pi$ charge transfer to the highest unoccupied MO ($4e(\pi^*)$).

We shall now discuss the electron configuration. The occurrence of π spin transfer suggests that the $d_{x^2-x^2}$ orbital is vacant and a lone electron occupies the (d_{xz}, d_{yz}) orbitals. The most probable electron configuration is $(d_{xy})^2 (d_{xz}, d_{yz})^3 (d_{zz})^2$. A lot of experimental data obtained by various methods agree with this configuration but some argue against it. A system with such a configuration has an S = 1/2 spin state. The EPR spectra at 77 K, which were first measured in ref. 10 and then in refs. 4, 15 and 19, correspond to the low-spin (S = 1/2)Fe(I). Comparison with isoelectronic d⁷ Co(II) porphyrins indicated lone electron localization in the d_{2} orbital. Both the disappearance of the EPR signal and the magnetic moment magnitude at higher temperature led at first to the proposal that the spin state changed to an S = 3/2 state at 200-300 K [3,10]. However, it was found by a subsequent study [3] that the samples used for the magnetic moment measurements in ref. 10 appear to be mixtures containing mostly high-spin Fe(II)P. When the samples were prepared with caution, a room temperature magnetic moment was found to be much closer to that expected of an S = 1/2system [3,15]. The changes in resonance Raman spectra on freezing the THF solution were assigned to the spin transition from 3/2 to 1/2 [19]. The authors [19] concluded that an unpaired electron occupied the $d_{x^2-v^2}$ orbital, which is inconsistent with our data.

We suggest the following explanation for these experimental observations. The NMR data at 300 K provide evidence for occupation of an extra electron in the (d_{xz}, d_{yz}) orbital. The magnetic moment measurements suggest an S = 1/2 state. The EPR results at 77 K are consistent with unpaired spin localization in the d_{z^2} orbital. If the unpaired spin occurs in the (d_{xy}, d_{yz}) orbital at high temperature and in the d_{z^2} orbital at low tem-

^aIn the case of pyrene π -dianions, a decrease in the total π electron density has been observed at the same positions that show a negative π spin density for π -radicals [48].

perature we have reason to assume that thermal migration of the lone electron from the d_{z^2} to the (d_{xy}, d_{yz}) orbital occurs on thawing of the frozen solution. Both the electron configurations $(d_{xy})^2(d_{xz}, d_{yz})^3(d_z)^2$ at 300 K and $(d_{xy})^2(d_{xz}, d_{yz})^4$ $(d_{z^2})^2$ at 77 K exhibit an S = 1/2 spin state. The (d_{xz}, d_{yz}) orbital can be higher in energy than d_{z^2} at 300 K in keeping with the intermediatespin Fe(II)P configuration. It may be assumed that the change in temperature results in a change in the relative energies of the (d_{xz}, d_{yz}) and d_{z^2} orbitals.

We shall now discuss the electronic structure of Fe(I) porphyrins in more detail. Fe \rightarrow P π^* charge transfer places the sizable π spin density in the highest unoccupied MO of the porphyrin. The occurrence of extra electron charge in the ligand MO implies a π -radical anion character of the Fe(I)P complex. The structural parameters, which have been derived from X-ray crystallography, provide independent evidence for π -radical formation [3,15]. Recently [49] we have studied π -radical anions, and π -anions of Zn and Mg porphyrin complexes in which metal atom reduction is unlikely, and extra electron charge resides in a ligand π HOMO. The results of our study [49] show that the change in the bond distances under reduction is consistent with the data reported in refs. 3 and 15. Thus, available data demonstrate [15] that the question of whether a redox reaction occurs at the iron atom or at the porphyrin ligand in [FeP]⁻ appears to have no simple answer. $P \rightarrow Fe$ π charge transfer suggests the reduction of iron. Alternatively, Fe \rightarrow P π spin transmission indicates the reduction of the ligand. Thus, in agreement with Mashiko et al. [15], such a reduced species may be thought of as a resonance hybrid of a d^7 Fe(I)P and an S = 1 d⁶ Fe(II) π -radical anion having sufficient metal/radical orbital overlap to give an overall S = 1/2 state:

 $[Fe(I)P]^{-} \leftrightarrow [Fe(II)P^{-}]^{-}$

The Fe(0) porphyrin ligand was also found to have π -anion character [3,15]. However, our NMR data give no evidence for this view.

G.N. Sinyakov and A.M. Shulga/J. Mol. Struct., 295 (1993) 1-14

| Table 6 | | | | | | | |
|-----------|--------|-------|----|-------|------------|----|--------------------|
| Isotropic | shifts | (ppm) | of | Fe(0) | porphyrins | in | THF-d ₈ |
| solution | | | | | | | |

| Compound | Isotropic shift | | | | | | |
|-------------|-----------------------------|----------------------------|---------------------------|----------------------------|----------------------------|--|--|
| | Pyrrole | | Meso | | | | |
| Fe(OEP) | α-CH ₂ 0.61 | β-CH ₃ -0.16 | H - 5.57 | | | | |
| Fe(TPrP) | Н — 2.78 | | α-CH ₂ 1.50 | β-CH ₂ -0.69 | γ-CH ₃ -0.39 | | |
| Fe(TPhP) | H - 2.93 | | <i>о</i> -Н — 0.95 | <i>т</i> -Н — 0.11 | <i>р</i> -Н — 0.16 | | |
| Fe(PhTMDEP) | H - 2.42 | | 15- H - 4.94 | 10,20-Н — 5.30 | | | |
| | α-CH ₂ 0.41 | β-CH ₃ -0.20 | <i>о</i> -Н — 0.69 | <i>т</i> -Н 0.08 | <i>р</i> -Н — 0.05 | | |
| | 2,8-CH ₃ 1,38 | | | | | | |
| | 12,18-CF 1,35 | ł ₃ | | | | | |

Iron(0) porphyrins

The isotropic shifts of Fe(0) porphyrins are listed in Table 6. The magnitudes of the isotropic shifts are too small to consider charge transfer. The maximum value of the meso H shift (-5.07 ppm) is ten times less than that in systems which exhibit spin transfer (high-spin Fe(III) and Fe(II)P, lowspin Fe(III)P, intermediate-spin Fe(II)P [2]). In general, ¹H NMR spectra of Fe(0) porphyrins are close to those of Fe(II)P in an S = 0 state and to diamagnetic Ni(II) porphyrins. The absorption spectra of d^8 Fe(0)P are similar to those of isoelectronic monoanion Co(II) porphyrins [Co(II)P]⁻ [8,50]. Fe(0)P, like [Co(II)P]⁻, is EPR inactive [4,15,19]. All these facts result in the conclusion that the most probable electron configuration is $(d_{xy})^2 (d_{xz} d_{yz})^4 (d_{zz})^2$.

Available data which suggest a π -anion character of the porphyrin ring of Fe(0)P [15] require an alternative explanation regarding NMR shift behavior. By analogy with the oxo-bridged dimers of Fe(III)P [2], the behavior of isotropic shifts may be indicative of iron and ligand ions coupled antiferromagnetically. To solve this question requires additional study. The chemical shifts of [CoP]⁻ can provide useful new information. We intend studying the NMR spectra of the reduced Co porphyrins, but we now restrict ourselves to the proposed explanations.

Conclusions

Analysis of the isotropic shifts of reduced iron porphyrins, Fe(II)P in an S = 0,1,2 state, Fe(I)Pand Fe(0)P, provide evidence for their electronic structure. The following was found.

(i) (a) Fe(II) porphyrins in pyridine solution (S = 0) do not exhibit any spin transfer. The electron configuration is $(d_{xy})^2 (d_{xz}, d_{yz})^4$.

(b) For Fe(II)P in benzene (S = 1), strong $P \rightarrow Fe \pi$ charge transfer occurs which agrees with an earlier study by La Mar et al. [32]. On the basis of the NMR shifts and Mössbauer data the proposal configuration is $(d_{xy})^2 (d_{z2})^2 (d_{xz}, d_{yz})^2$.

(c) The contact shifts of high-spin ferrous porphyrin in THF (S = 2) are consistent with Fe \rightarrow P σ spin transfer. The most probable electron configuration is $(d_{xy})^2(d_{xz},d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^1$. The pattern of the shifts reflects the difference between complexes of Fe(II)P with THF and those with 2-MeIm [33], which accounts for the difference in bonding THF and 2-MeIm with iron.

(ii) The contact shifts of Fe(I) porphyrins indicate negative π spin density on the pyrrole and meso carbon atoms due to a strong π - π spin polarization effect. When the negative sign of the π spin density is neglected, the pattern of contact shift suggests sizable Fe \rightarrow P π^* charge transfer and P \rightarrow Fe π charge transfer. The former indicates a π -radical anion character of the porphyrin ligand, which is consistent with available data from X-ray crystallographic analysis [3,15]. The ground state is probably $(d_{xy})^2(d_{xz}, d_{yz})^3(d_{z2})^2$.

(iii) The small isotropic shifts of Fe(0) porphyrins give no evidence for any charge transfer. The proposed electron configuration is $(d_{xy})^2$ $(d_{xz},d_{yz})^4(d_{z2})^2$. The NMR data disagree with X-ray crystallographic analysis which suggests a π -radical anion formulation for the Fe(0) porphyrins [3,15].

References

- 1 W.R. Scheidt and C.A. Reed, Chem. Rev., 81 (1981) 543.
- 2 G.N. La Mar and F.A. Walker, in D. Dolphin (Ed.), The Porphyrins, Vol. 4, Academic Press, New York, 1979, pp. 61–157.
- 3 C.A. Reed, Adv. Chem. Ser., 201 (1982) 333.
- 4 D. Lexa, M. Momenteau and J. Mispelter, Biochem. Biophys. Acta, 338 (1974) 151.
- 5 K.M. Kadish, G. Larson, D. Lexa and M. Momenteau, J. Am. Chem. Soc., 97 (1975) 282.
- H. Kobayashi and Y. Yanagava, Bull. Chem. Soc. Jpn., 45 (1972) 450.
- 7 D. Brault and M. Rougee, Biochemistry, 13 (1974) 4598.
- 8 V.G. Maslov, T.P. Prokof'eva and A.N. Sidorov, Zh. Fiz. Khim., 62 (1988) 2239.
- 9 D. Brault and M. Rougee, Biochemistry, 13 (1974) 4591.
- 10 J.A. Cohen, D. Ostfeld and B. Lichtenstein, J. Am. Chem. Soc., 94 (1972) 4522.
- 11 J.P. Collman, J.L. Hoard, N. Kim, G. Long and C.A. Reed, J. Am. Chem. Soc., 97 (1975) 2676.
- 12 L.J. Radonovich, A. Bloom and J.L. Hoard, J. Am. Chem. Soc., 94 (1972) 2073.
- 13 J.P. Collman and C.A. Reed, J. Am. Chem. Soc., 95 (1973) 2048.
- 14 C.A. Reed, T. Mashiko, W.R. Scheidt, K. Spartalian and G. Lang, J. Am. Chem. Soc., 102 (1980) 2302.
- 15 T. Mashiko, C.A. Reed, K.J. Haller and W.R. Scheidt, Inorg. Chem., 23 (1984) 3192.
- 16 P. Hambright and A. Bearden, in K.M. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1975, p. 539.
- 17 O. Medhi and J. Silver, J. Chem. Soc., Chem. Commun., 17 (1989) 1199.
- 18 T.G. Spiro, in A.B.P. Lever and H.B. Gray (Eds.), Iron Porphyrins, Vol. 2, Addison-Wesley, London, 1983, p. 91.
- 19 J. Teraoka, S. Hashimoto, H. Sugimoto, M. Mori and T. Kitagava, J. Am. Chem. Soc., 109 (1987) 180.
- 20 A.R. Battersby, D.G. Buckley, S.G. Hartley and M.D. Turnbull, J. Chem. Soc., Chem. Commun. (1976) 879.
- 21 J.E. Baldvin, T. Klose and M. Peters, J. Chem. Soc., Chem. Commun. (1976) 881.
- 22 M. Momenteau, B. Loock and E. Bisagni, Can. J. Chem., 57 (1979) 1804.
- 23 J.T. Landrum, K. Hotano, W.R. Scheidt and C.A. Reed, J. Am. Chem. Soc., 102 (1980) 6729.
- 24 L.M. Epstein, D.K. Straub and C. Maricondi, Inorg. Chem., 6 (1967) 1720.

- 25 E.V. Goldmayer and H. Zorn, J. Magn. Reson., 23 (1976) 199.
- 26 D.L. Budd, G.N. La Mar, K.C. Langry, K.M. Smith and R. Nayyir-Mazhir, J. Am. Chem. Soc., 101 (1979) 6091.
- 27 K. Wüthrich and R. Baumann, Helv. Chim. Acta, 56 (1973) 595.
- 28 M. Wicholas, R. Mustacich and D. Jaune, J. Am. Chem. Soc., 94 (1972) 4518.
- 29 W.S. Caughey, C.H. Barlow, D.H. O'Keeffe and M.C. O'Tool, Ann. N.Y. Acad. Sci., 206 (1973) 296.
- 30 F.A. Walker and G.N. La Mar, Ann. N.Y. Acad. Sci., 206 (1973) 328.
- 31 G.N. La Mar and F.A. Walker, J. Am. Chem. Soc., 95 (1973) 1782.
- 32 H. Goff, G.N. La Mar and C.A. Reed, J. Am. Chem. Soc., 99 (1977) 3641.
- 33 H. Goff and G.N. La Mar, J. Am. Chem. Soc., 99 (1977) 6599.
- 34 G.N. La Mar, E.R. Eaton, R.H. Holm and F.A. Walker, J. Am. Chem. Soc., 95 (1973) 63.
- 35 A.M. Shulga and G.V. Ponomaryov, Khim. Geterotsikl. Soedin., 7 (1984) 922.
- 36 A.D. Adler, F.R. Longo, J. Goldmacher, J. Assour and L. Korsakoff, J. Org. Chem., 32 (1967) 476.
- 37 A. Treibs and N. Häberle, Lieb. Ann. Chem., 718

(1968) 183.

- 38 A.M. Shulga and G.P. Gurinovich, Dokl. Akad. Nauk B. SSR, 25 (1981) 55.
- 39 A.D. Adler, F.R. Longo, F. Kampas and J. Kim, J. Inorg. Nucl. Chem., 32 (1970) 2443.
- 40 G.L. Closs and L.E. Closs, J. Am. Chem. Soc., 85 (1963) 818.
- 41 A.N. Sidorov and V.G. Maslov, Usp. Khim., 44 (1975) 517.
- 42 H.M. McConnel and R.E. Robertson, J. Chem. Phys., 29 (1958) 1361.
- 43 F.A. Walker, Tetrahedron Lett., 52 (1971) 4949.
- 44 G.N. La Mar and F.A. Walker, J. Am. Chem. Soc., 97 (1975) 5103.
- 45 C. Lecomte, R.H. Blessing, P. Coppens and A. Tabard, J. Am. Chem. Soc., 108 (1986) 6942.
- 46 A.D. McLachlan, Mol. Phys., 3 (1960) 233.
- 47 G.J. Hoijtink, J. Towsend and S.I. Weissman, J. Chem. Phys., 34 (1961) 507.
- 48 I.V. Filatov, G.N. Sinyakov, A.M. Shulga and G.P. Gurinovich, Zh. Strukt. Khim., 31 (1990) 70.
- 49 G.P. Gurinovich, I.F. Gurinovich, N.V. Ivashin, G.N. Sinakov, A.M. Shulga, S.N. Terekhov, I.V. Filatov and K. Dzilinski, J. Mol. Struct., 172 (1988) 317.
- 50 S.N. Terekhov and I.F. Gurinovich, Teor. Eksp. Khim., 18 (1982) 503.