Figure 5. Components used to simulate the ^{77}Se NMR spectrum of $Te_2Se_6^{2+}$, 77.3% enriched in ^{125}Te, natural-abundance ^{77}Se.

observed satellites accounted for. AA'X and AA'XX' systems have been reported, for example, in the ^{1}H spectrum of 2-furfurol[17] and the ^{19}F spectrum of 1,2-dichloro-3,4,5,6-tetra-fluorobenzene,[18] but to our knowledge this is the first report of such inequivalence involving heavy nuclei.

The ^{77}Se NMR spectrum of this same sample complements the above analysis (Figure 4). The simulated spectrum incorporates the X portions of the coupling patterns described above as well as X, X_2, AXX', and AX_2 components (Table III). The individual components used in the simulation are displayed in Figure 5. The signal-to-noise ratio in the observed spectrum is not good enough to determine any ^{77}Se–^{77}Se couplings, and the estimates used in the ^{125}Te simulation are retained here. The simulated ^{77}Se spectrum matches the observed spectrum when a line width of 30 Hz is used in the simulation.

Conclusions

The results of this ^{77}Se and ^{125}Te NMR investigation of the $Te_2Se_6^{2+}$ cation are consistent with retention in solution of the solid-state arrangement of two tellurium atoms joined by three, two-atom selenium chains. An important feature of the solid-state structure is the large Te–Se–Se–Te dihedral angle of 69°. The resulting interchain Se–Se distances are significantly shorter than twice the van der Waals radius of Se. These may therefore be weak bonding interactions.[11] Similar short interchain distances are observed in the $Te_2Se_8^{2+}$ cation[11] and the isostructural Se_{10}^{2+} cation.[8] Vicinal ^{1}H–^{1}H couplings in HCCH fragments are dependent upon the H–C–C–H dihedral

angle.[19] The observed ^{125}Te–^{125}Te coupling for $Te_2Se_6^{2+}$ could, in principle, be of significance in deducing the Te–Se–Se–Te dihedral angle in solution, but since no other ^{125}Te–^{125}Te couplings have been reported for similar geometries, no correlation between the coupling constant and the dihedral angle can be established at present.

(19) Harris, R. K.; Sheppard, N. *Trans. Faraday Soc.* **1963**, *59*, 606.

Proton NMR Studies on Six-Coordinated "High-Spin" Iron(III) Porphyrins

D. V. Behere, R. Birdy, and S. Mitra*

High-spin ferric ion in heme proteins generally occurs as six-coordinated while the corresponding iron(III) porphyrins are often five-coordinated. In order to find better synthetic models for the heme proteins, there has recently been con-

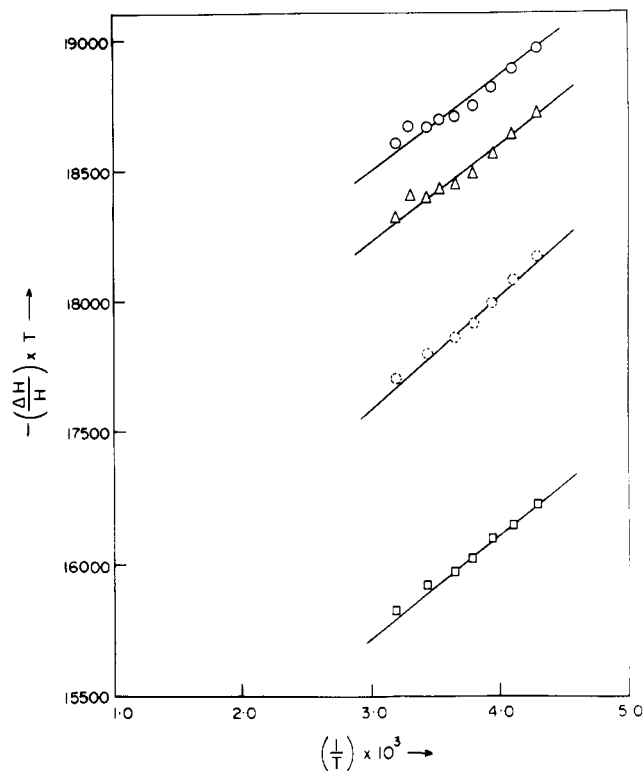(17) Abraham, R. J.; Bernstein, H. J. *Can. J. Chem.* **1961**, *39*, 216.
(18) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: Oxford, 1965; Vol. 1.
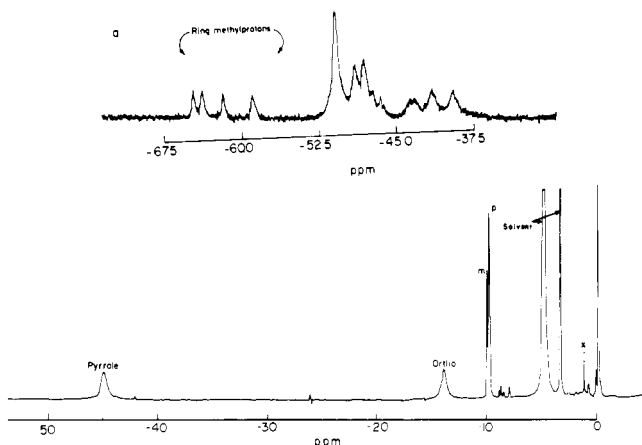
Figure 1. Proton NMR traces for the six-coordinated iron(III) porphyrins. For the protoporphyrin complex (a) only the relevant part of the spectrum is shown; the lower trace is shown for Fe(TP-P)(CD$_3$OD)$_2$(ClO$_4$).

siderable interest in stabilizing and isolating six-coordinated high-spin iron(III) porphyrins by using weak-field axial ligands (L), such as alcohol and dimethyl sulfoxide.[1-4] The existence of six-coordinated high-spin species has been established in solution by NMR[1-4] and in the solid state by X-ray crystallography.[5,6] In particular, the NMR studies have shown that when a five-coordinated ferric porphyrin, such as Fe(Por)X (X = Cl, Br, etc.) is dissolved in methanol or Me$_2$SO (L), the six-coordinated species, Fe(Por)L$_2$, is formed.[2-4] The magnetic moment of these species, measured in solution by the NMR method, is generally 5.9 ± 0.3 μ_B, which is considered indicative of their high-spin state. An attempt was made some years ago to deduce the electronic structure of the high-spin ferric ion in these six-coordinated species by temperature-dependent proton NMR studies in a solution of Me$_2$SO. Owing to the relatively high freezing point of the solvent, the measurements could therefore be done only over a restricted range of temperatures (330–285 K) and were not very useful for the purpose of the study. Since these six-coordinated iron(III) porphyrins have been suggested as models for aquometmyoglobin,[2,3] it is important that the electronic structure of the iron in these models is accurately known. No such information is currently available on these species stabilized in solution.

As a part of a continuing interest in the electronic structure of metalloporphyrins,[7-10] we decided to carry out a detailed NMR study on six-coordinated species stabilized in solution. We report here our proton NMR study over a wider range of temperatures on two six-coordinated iron(III) porphyrins, namely Fe(PP)Cl in Me$_2$SO-d_6 and Fe(TPP)ClO$_4$ in CD$_3$OD, where PP and TPP are the protoporphyrin and tetraphenyl-

(1) Kurland, R. J.; Little, R. G.; Davis, D. G.; Ho, C. *Biochemistry* **1971**, *10*, 2237.
(2) Morishima, I.; Kitagawa, S.; Matsuki, E.; Inubushi, T. *J. Am. Chem. Soc.* **1980**, *102*, 2429.
(3) Budd, D. L.; LaMar, G. N.; Langry, K. C.; Smith, K. M.; Nayyir-Mazhir, R. *J. Am. Chem. Soc.* **1979**, *101*, 6091.
(4) Zobrist, M.; LaMar, G. N. *J. Am. Chem. Soc.* **1978**, *100*, 1944.
(5) Kastner, M. E.; Scheidt, W. R.; Mashiko, T.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 666.
(6) Mashiko, T.; Kastner, M. E.; Spartalian, K.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 6354.
(7) Behere, D. V.; Marathe, V. R.; Mitra, S. *J. Am. Chem. Soc.* **1977**, *99*, 4149.
(8) (a) Behere, D. V.; Mitra, S. *Inorg. Chem.* **1979**, *18*, 1723. (b) Behere, D. V.; Date, S. K.; Mitra, S. *Chem. Phys. Lett.* **1979**, *68*, 544. (c) Behere, D. V.; Mitra, S. *Indian J. Chem., Sect. A* **1980**, *19A*, 505. (d) Birdy, R.; Behere, D. V.; Mitra, S. *J. Chem. Phys.* **1983**, *78*, 1453. (e) Marathe, V. R.; Mitra, S. *Ibid.* **1983**, *78*, 915.
(9) Behere, D. V.; Birdy, R.; Mitra, S. *Inorg. Chem.* **1982**, *21*, 386.
(10) Behere, D. V.; Mitra, S. *Proc.—Indian Acad. Sci., Sect. A* **1982**, *91A*, 145.

Figure 2. Temperature-dependent isotropic proton shifts for the four methyl protons in Fe(PP)(Me$_2$SO)$_2$Cl. The solid lines are theoretical ones for D = 8.4 ± 0.3 cm^{-1} and A_s = 0.1 ± 0.01 MHz.

porphyrin dianions, respectively. The presence of [Fe(PP)-(Me$_2$SO)$_2$]$^+$ in the former has already been established,[1,2] and the existence of [Fe(TPP)(CD$_3$OD)$_2$]$^+$ in the latter can be inferred from the proton NMR observation that the analogous Fe(OEP)ClO$_4$ coordinates to two solvent molecules in methanol, forming six-coordinated [Fe(OEP)(CD$_3$OD)$_2$]$^+$ species.[2]

Experimental Details

The samples were prepared by previous methods. [Fe(PP)-(Me$_2$SO)$_2$]Cl was obtained by dissolving about 2–3 mg of hemin chloride in a minimum amount of Me$_2$SO-d_6 and then diluting the resulting solution to about 1 mL in CDCl$_3$. This enabled us to extend the temperature range of NMR measurements down to ca. 220 K. Similarly, [Fe(TPP)(CD$_2$OD)$_2$]$^+$(ClO$_4$)$^-$ was obtained in solution by dissolving Fe(TPP)ClO$_4$ in a mininum amount of CDCl$_3$ and then diluting the resulting solution with excess of CD$_3$OD.
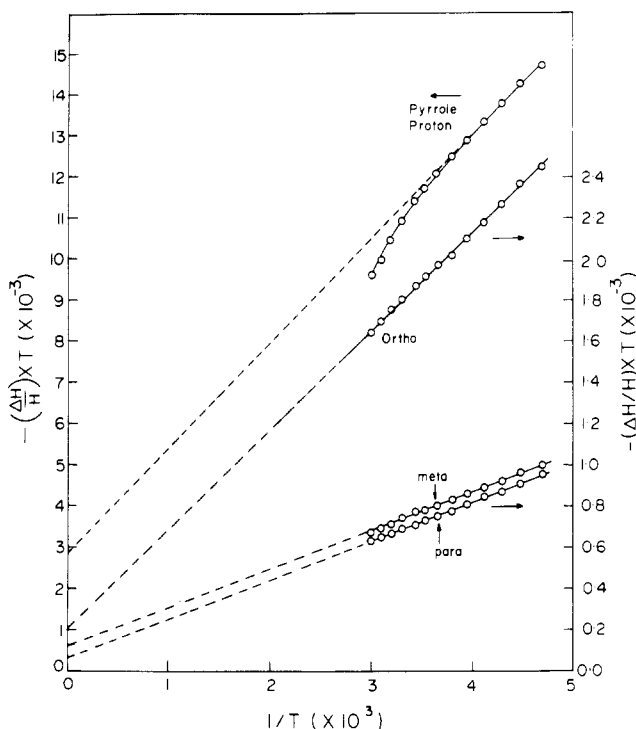
Results

The traces of the proton NMR spectra of the compounds at room temperature are shown in Figure 1. The spectrum of [Fe(PP)(Me$_2$SO-d_6)$_2$]$^+$ agrees very well with the previously reported one,[3] and our assignment of the four ring methyl protons is based on this work. The resonances due to the methyl protons are well separated and sharp and hence convenient for theoretical analysis. The pyrrole proton resonance in the spectrum of [Fe(TPP)(CD$_3$OD)$_2$]$^+$ can be easily identified on the basis of the reported spectra of Fe(TPP)X (X = Cl, Br, etc.) and [Fe(TPP)(Me$_2$SO-d_6)$_2$]$^+$.[1,2,9] Some of the relevant assignments are shown in Figure 1. The observed isotropic shifts were corrected for the diamagnetic shift by using the corresponding zinc(II) porphyrin data. The temperature dependence of the corrected isotropic proton shifts (IPS) is shown in Figures 2 and 3. The data have been plotted as (IPS × T) vs. 1/T for reasons which will become clear below.

Discussion

The IPS consists of contact and dipolar terms:

$$\left(\frac{\Delta H}{H}\right)_{\text{IPS}} = \left(\frac{\Delta H}{H}\right)_{\text{CS}} + \left(\frac{\Delta H}{H}\right)_{\text{DS}} \qquad (1)$$

Figure 3. Temperature-dependent isotropic proton shifts for Fe(T-PP)(CD₃OD)₂(ClO₄). The solid lines are calculated ones. See the text for the parameters. For pyrrole protons, hyperfine coupling constants $A_s(^5/_2) = -0.27 \pm 0.03$ MHz and $A_s(^3/_2) = 1.7 \pm 0.3$ MHz were deduced.

For a high-spin iron(III) porphyrin with a $^6A_1$ ground electronic state, the expressions for contact and dipolar shifts, which have been deduced by Kurland and McGarvey,[11] are

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

$$\left(\frac{\Delta H}{H}\right)_{DS} = \frac{28g^2\beta^2}{9k^2T^2}\left\langle\frac{3\cos^2\theta - 1}{r^3}\right\rangle D \qquad (3)$$

Here A_s is the hyperfine coupling constant and $\langle(3\cos^2\theta - 1)/r^3\rangle$ is the geometric factor as defined elsewhere.[9,12] D is the zero-field splitting parameter of the ground state and is sensitive to stereochemical changes around the iron.[13,14] If we combine eqs 2 and 3, eq 1 can be written as

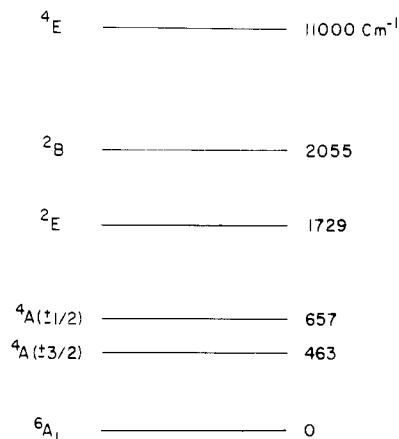$$\left(\frac{\Delta H}{H}\right)_{IPS} = a/T + b/T^2 \qquad (4)$$

where

$$a = -\frac{35g\beta}{12(\gamma_H/2\pi)k}\left(\frac{A_s}{h}\right)$$

$$b = \frac{28g^2\beta^2}{9k^2}\left\langle\frac{3\cos^2\theta - 1}{r^3}\right\rangle D$$

A plot of $(\Delta H/H)_{IPS}T$ vs. $1/T$ should give a straight line for high-spin iron(III) systems, its slope and intercept determining D and A_s, respectively. In Figures 2 and 3 such plots are shown for the methyl protons of [Fe(PP)(Me₂SO-d_6)₂]⁺ and the pyrrole and phenyl protons of [Fe(TPP)(CD₃OD)₂]⁺.

The data in Figure 2 show a very rigorously high-spin behavior for the six-coordinated protoporphyrin species. The

(11) Kurland, R. J.; McGarvey, B. R. *J. Magn. Reson.* **1970**, *2*, 286.
(12) LaMar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63.
(13) Mitra, S. *Prog. Inorg. Chem.* **1977**, *22*, 307.
(14) Behere, D. V.; Birdy, R.; Mitra, S. *Inorg. Chem.* **1981**, *20*, 2786.

Figure 4. Energy-level scheme in Fe(TPP)(CD₃OD)₂ClO₄ as deduced from the NMR data.

experimental shifts for the four methyl protons lie very close together on four different straight lines that are nearly parallel to each other, satisfying eq 4 very strictly. From the slope of each straight line a value of D can be calculated, which gives $D = 8.1, 8.3, 8.1$, and 8.7 cm⁻¹, leading to an average value of $D = 8.3$ cm⁻¹. The intercepts likewise give an average value of $A_s = 0.1 \pm 0.01$ MHz. The zero-field splitting in this six-coordinated complex is thus larger than that in the parent hemin chloride (6.9 cm⁻¹),[15] and is evidently due to the axial Me₂SO coordination. That the axial Me₂SO coordination increases the zero-field splitting of the ground state is also observed[5] in [Fe(TPP)(Me₂SO)₂]⁺Cl⁻, which shows $D = 10$ cm⁻¹ as against $D = 6.0$ for the parent Fe(TPP)Cl.[9] A comparison of the zero-field splitting in [Fe(PP)(Me₂SO)₂] with that in heme proteins shows that there is in fact no close agreement between them ($D = 11$ and 7 cm⁻¹ for aquomet-myoglobin and aquomethemoglobin, respectively[16,17]). This is however not surprising since the nature of axial bonding in the two cases is not the same, and zero-field splitting is very sensitive to even minor changes in the chemical environment.

The temperature dependence of the IPS for the pyrrole proton shows marked deviation, especially at higher temperatures, from the linearity necessary for $S = ^5/_2$ spin state (Figure 3). Moreover, the magnitude of the IPS is considerably smaller than that in the known examples of high-spin iron(III) porphyrins. For example, at 200 K the shift for the pyrrole proton in [Fe(TPP)(CD₃OD)₂]⁺ is −66 ppm as compared to −120 and −101 ppm in high-spin Fe(TPP)I and [Fe(TPP)(Me₂SO)₂]⁺, respectively.[9] There are two possible explanations for the kind of deviation observed in Figure 3. One is chemical exchange between the coordination of the perchlorate and the methanol. However, since an excess of methanol was used in the experiment, this exchange can be ruled out, and the species present in the solution is ensured to be the bis(methanol) adduct. The second possibility, which appears to be the most likely one, is that the ground state of the ferric ion in this complex is not pure high spin but may be spin mixed with some low-lying excited state of appropriate symmetry.

For a ferric ion in tetragonal symmetry there are several possible low-lying excited states ($^2B_2$, ^2E, ^4E, and $^4A_2$) that can mix directly or indirectly with the ground state $^6A_1$ via spin–orbit coupling.[18,19] This mixing has been calculated very

(15) Richards, P. L.; Caughey, W. S.; Eberspaecher, H.; Feher, G.; Malley, M. *J. Chem. Phys.* **1967**, *47*, 1187.
(16) Venoyama, H.; Iizyka, T.; Morimoto, H.; Kotani, M. *Biochim. Biophys. Acta* **1968**, *160*, 159.
(17) Kotani, M. *Ann. N.Y. Acad. Sci.* **1969**, *158*, 20.
(18) Marathe, V. R.; Mitra, S. *Indian J. Pure Appl. Phys.* **1976**, *14*, 893.
(19) Harris, G. M. *Theor. Chim. Acta* **1968**, *10*, 119, 155.

rigorously in a crystal field model which parametrizes the crystal field splitting in terms of three parameters: Δ, the total cubic field splitting of the b_1 and b_2 orbitals, and δ_1 and δ_2, the tetragonal splitting of the t_{2g} and e_g orbitals.[18] The isotropic proton shifts can then be calculated within this model in a manner as described by Gregson.[20] By the use of the free-ion values of Racah and spin–orbit coupling parameters the data in Figure 3 can be best fitted for $\Delta = 33\,100$ cm^{-1}, $\delta_1 = 1250$ cm^{-1}, and $\delta_2 = 12\,500$ cm^{-1}. This gives an energy-level scheme as shown in Figure 4. While the exact values of the energies would be dependent on the choice of the Racah and spin–orbit coupling parameters, their relative values are realistic, giving credence to the relative ordering of the energy levels. The low-lying $^4A_2$ state mixes very substantially into the ^6A state, producing a spin-mixed ground state with 68% $^6A_1$ ($\pm^1/_2$) and ca. 31% $^4A_2$ ($\pm^3/_2$), the contribution of all other states being not more than 1%. The features of the electronic structure are interesting. First, several ferric heme proteins and porphyrins show spin-state mixing and are known to have a $^6A_1$ and $^4A_2$ spin-mixed ground state.[14,21–26] In some cases[21,24] the ground state is predominantly $^6A_1$; in others, the latter.[22,26] Second, ^2E, not ^4E, lies immediately above $^4A_2$. ^4E in fact lies very high in energy, which appears to be a common feature in iron(III) porphyrins.[8d,19]

For the phenyl protons, the isotropic shifts are very small and the contact terms are only about 10% of the IPS. Since the spin-state mixing will affect predominantly only the contact term, its effect is not apparent in the temperature dependence of the phenyl protons, hence the linear variation in Figure 3.

Conclusion

The present work has shown that when weak axial ligands such as Me$_2$SO or alcohols coordinate to iron(III) porphyrins, forming six-coordinated iron(III) porphyrins, these six-coordinated porphyrins are not always high spin. A careful temperature-dependent NMR study is important to establish the nature of the ground electronic state of the metal ion.

(20) Gregson, A. K. *Inorg. Chem.* **1981**, *20*, 81.
(21) Mitra, S.; Date, S. K.; Nipankar, S. V.; Birdy, R.; Girerd, J. J. *Proc.—Indian Acad. Sci., Sect. A* **1980**, *89A*, 511.
(22) Mitra, S.; Marathe, V. R.; Birdy, R. *Chem. Phys. Lett.* **1983**, *96*, 103.
(23) Maltempo, M. M. *J. Chem. Phys.* **1974**, *61*, 2540.
(24) Maltempo, M. M.; Moss, T. H.; Cusanovich, M. A. *Biochim. Biophys. Acta* **1974**, *342*, 290.
(25) Dolphin, D. H.; Sams, J. R. Tsin, I. B. *Inorg. Chem.* **1977**, *16*, 711.
(26) Reed, C. A.; Mashiko T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R. *J. Chem. Soc* **1979**, *101*, 2948.

Contribution from the Instituto de Fisica
e Quimica de Sao Carlos, University of Sao Paulo,
13560 Sao Carlos S.P., Brazil,
and Department of Chemistry, University of Calgary,
Calgary, Alberta, Canada T2N 1N4

Electronic Spectrum of the Planar S$_4$N$_3^+$ Cation

M. Trsic[†] and W. G. Laidlaw*[‡]

The planar ring structure of the S$_4$N$_3^+$ cation has been known for almost 2 decades,[1] and early studies were directed to the interpretation of its electronic spectrum and structure.[2–5] In a recent work Waluk and Michl[6] reported its magnetic

[†] University of Sao Paulo.
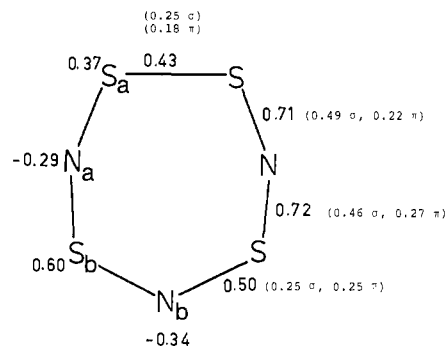[‡] University of Calgary.

Figure 1.

circular dichroism (MCD) spectrum. The MCD results indicate that each of the two electronic bands, at 340 and 263 nm, respectively, consists of two pairs of nearly degenerate transitions.

We have employed the Hartree–Fock–Slater (HFS) method, which is well documented in the literature[7] and widely used for sulfur nitrides[8] in order to elucidate the nature of these transitions. The calculation was performed in terms of a double-ζ basis augmented with a 3d polarization function on sulfur. The experimental geometry[1] was suitably averaged to C_{2v} symmetry.

The 38-electron single-determinant ground state that we obtained can be represented by $(1a_1)^2(1b_1)^2(2a_1)^2(2b_1)^2$-$(3a_1)^2(3b_1)^2(4a_1)^2(5a_1)^2(1b_2)^2(4b_1)^2(1a_2)^2(6a_1)^2(2b_2)^2(5b_1)^2$-$(7a_1)^2(6b_1)^2(3b_2)^2(2a_2)^2(8a_1)^2$ where the orbitals are arranged in ascending energy. The energy of the two highest occupied π orbitals $3b_2$ and $2a_2$ were respectively –0.432 and –0.429 au while the two lowest unoccupied orbitals $3a_2$ and $4b_2$ had energies of –0.310 and –0.282 au, respectively.

The calculated electronic transitions were obtained from the difference between one-electron HFS eigenvalues shifted by a constant 0.40 eV; this procedure has been shown to be quite adequate for other sulfur nitrides[9] and has been given theoretical justification recently.[10] The experimental electronic spectrum contains two bands, one at 340 nm and another at 263 nm. Our calculations show that the 340-nm band appears to be produced by the almost degenerate $2a_2 \rightarrow 3a_2$ and $3b_2 \rightarrow 3a_2$ transitions whereas the 263-nm band is a result of the $2a_2 \rightarrow 4b_2$ and $3b_2 \rightarrow 4b_2$ transitions. The values given by the MCD analysis of Waluk and Michl of 28 500 and 30 500 cm^{-1} or 351 and 328 nm correspond well with the calculated pair at 341 and 332 nm. Michl's values of 267 and 250 nm are also in reasonably good agreement with the calculated pair at 282 and 277 nm. All four orbitals involved in these transitions, i.e., $3b_2$ (the HOMO – 2), $2a_2$ (HOMO – 1), $3a_2$ (LUMO), and $4b_2$ (LUMO + 1), are of π symmetry, and this

(1) (a) J. Weiss, *Z. Anorg. Allg. Chem.*, **333**, 314 (1964); (b) A. W. Cordes, R. F. Kruh, and E. K. Gordon, *Inorg. Chem.*, **4**, 681 (1965).
(2) D. A. Johnson, G. D. Blyholder, and A. W. Cordes, *Inorg. Chem.*, **4**, 1790 (1965).
(3) P. Friedman, *Inorg. Chem.*, **8**, 692 (1969).
(4) R. D. Harcourt, *J. Inorg. Nucl. Chem.*, **39**, 237 (1977).
(5) D. B. Adams, A. J. Banister, D. T. Clark, and D. Kilcast, *Int. J. Sulfur Chem., Part A*, **1**, 143 (1971).
(6) J. W. Waluk and J. Michl, *Inorg. Chem.*, **21**, 556 (1982).
(7) (a) E. J. Baerends and P. Ros, *Intl. J. Quantum Chem. Symp.*, **12**, 169 (1978); (b) E. J. Baerends, E. D. Ellis, and P. Ros, *Chem. Phys.*, **2**, 41 (1973).
(8) (a) J. Bojes, T. Chivers, W. G. Laidlaw, and M. Trsic, *J. Am. Chem. Soc.*, **101**, 4517 (1979); (b) N. Burford, T. Chivers, A. W. Cordes, W. G. Laidlaw, M. C. Noble, R. T. Oakley, and P. N. Swepston, *ibid.*, **104**, 1282 (1982); (c) T. Chivers, P. W. Codding, W. G. Laidlaw, S. W. Liblong, R. T. Oakley, and M. Trsic, *ibid.*, **105**, 1186 (1983).
(9) (a) M. Trsic, K. Wagstaff, and W. G. Laidlaw, *Int. J. Quantum Chem.*, **22**, 903 (1982); (b) M. Trsic, W. G. Laidlaw, and R. T. Oakley, *Can. J. Chem.*, **60**, 2281 (1982).
(10) M. Trsic and W. G. Laidlaw, *Int. J. Quantum Chem., Quantum Chem. Symp.*, **17**, 367 (1983).