Extended Hückel Calculations of Hydrogen and Nitrogen Electron Paramagnetic Resonance Coupling Constants for σ Radicals Containing Carbon, Hydrogen, Nitrogen, and Oxygen Atoms

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Abstract: We have been able to calculate the hydrogen and nitrogen epr coupling constants for a series of σ radicals containing nitrogen and oxygen. The hydrogen coupling constants are calculated by a method previously reported, while the nitrogen coupling constants are evaluated using a double-scale equation with empirical constants to convert the calculated eigenvector coefficients for the nitrogen 2s and 2p orbitals to the coupling constants, *i.e.*, A_N (G) $= 1425(C_{2s})^2 + 12.01(C_{2p_x}{}^2 + C_{2p_y}{}^2 + C_{2p_z}{}^2)$. The usefulness of these calculations in assigning epr spectra is discussed.

Recently there have been several attempts to calculate the isotropic epr hyperfine coupling constants of σ radicals by using a semiempirical approach.[2-5] In general, these calculations have met with rather surprising success. One of our longer range goals in this research is to interpret mechanisms of spin delocalization in paramagnetic transition metal ion complexes, manifested by nmr contact shifts. Therefore, we decided to extend our investigation of hydrocarbon σ radicals to include radicals which contain the heteroatoms nitrogen and oxygen, and thus are more like the ligands encountered in transition metal coordination chemistry. To this end we chose to examine some simple radicals whose coupling constants have been experimentally determined.[6,7] We also decided to test the ability to predict the magnitude of the nitrogen hyperfine interaction from our calculated wave functions.

It was of interest to ascertain whether or not the choice of parameters previously employed on a series of hydrocarbons could also be applied to radicals containing the heteroatoms nitrogen and oxygen. The additional possibility of calculating the nitrogen hyperfine interaction from our ground-state wave function also made these radicals of particular interest.

Methods and Parameters

The calculations were carried out as previously described.[2,8] Briefly, the Coulomb integrals, H_{ii}, were approximated by the valence-state ionization potentials (VSIP) of Hinze and Jaffé[9] and corrected for charge by Cusachs' parameters.[10] The off-diagonal elements, H_{ij}, were calculated according to the Wolfsberg–Helmholz arithmetic mean[11] with $K = 1.75$. Orbital exponents were calculated according to Slater's rules.[12] In order to minimize computer time, the orbital exponents were, in general, not corrected for charge. This was found to introduce a small error (<5%) in the value of the calculated coupling constant. The hydrogen exponent was set at 1.2.

The hydrogen coupling constants were calculated by evaluating the square of the total value of the wave function of the molecular orbital containing the unpaired electron at the nucleus and then multiplying by the scaling factor 1887 G obtained from the hydrocarbon work.[3] Thus

$$A_{\mathrm{H}} = 1887\psi(0)^2 \qquad (1)$$

where A_{H} is given in gauss.

Since Slater 2s orbitals, with their troublesome node at the nucleus, were used in these calculations, no attempt was made to evaluate the total value of ψ of the MO at the nitrogen nucleus. In the case of nitrogen, it is a good approximation to use only the coefficients of the nitrogen atomic orbitals in calculating the hyperfine coupling constants instead of the total value of ψ of the MO at the nucleus which is often necessary for hydrogen atoms in σ molecular orbitals.[2] This results because neighbor atoms produce a relatively small contribution to the total value of $\psi(0)$ in the case of nitrogen. The value of $\psi(0)$ for a hydrogen atom Slater 1s orbital is $(0.178/a_0{}^{3/2})$, while that calculated for a Clementi analytical nitrogen 2s orbital is $(2.18/a_0{}^{3/2})$. Since coefficients of hydrogen 1s and nitrogen 2s orbitals in the MO's are on the order of 0.1–0.2, values of $\psi(0)$ from $0.0178/a_0{}^{3/2}$ to $0.0356/a_0{}^{3/2}$ for hydrogen and from $0.218/a_0{}^{3/2}$ to $0.436/a_0{}^{3/2}$ for nitrogen are observed. Contributions at a nucleus from atomic orbitals on other centers in the molecule are often $0.01/a_0{}^{3/2}$, which is significant in the hydrogen case, but which can safely be ignored in the nitrogen case.

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The isotropic nitrogen coupling constants were calculated from the relation

$$A_N = A(C_{2s})^2 + B(C_{2p_x}^2 + C_{2p_y}^2 + C_{2p_z}^2) \qquad (2)$$

where C_{2s} is the coefficient of the nitrogen 2s orbital and C_{2p_x}, C_{2p_y}, and C_{2p_z} are the coefficients of the nitrogen $2p_x$, $2p_y$, and $2p_z$ orbitals in the MO containing the unpaired electron. The empirical constants A and B are scaling factors, with A representing the direct Fermi contact term, and with B representing additional contact due to spin polarization of the electrons in 1s and 2s orbitals by unpaired electrons in the nitrogen 2p orbitals. The formulas of the compounds considered are reported in Table I. The methylenimino calculation resulted in placing the unpaired electron in an orbital containing only N_{2p_y}, C_{2p_y} and H_{1s} coefficients, but no N_{2s} coefficient for symmetry reasons. Hence, for this radical, eq 2 simplifies to one unknown, and, using the value of the nitrogen coupling constant measured by Cochran, *et al.*,[13] we find $B = 12.01$ G. Then, using this calculated value for B and the experimental value for the nitrogen coupling constant of *syn*-benzaldoxime,[7] we were able to solve for A, which was found to be 1425 G. It should be noted that a calculation using Clementi's SCF analytical orbitals in the 2-pyridyl radical yielded a value of 1419 G for A.

The geometries used in this work are as follows.

(1) For *syn*- and *anti*-benzaldoxime radicals, the bond lengths and angles were those determined by Jerslev[14] for *syn*- and *anti*-*p*-chlorobenzaldoxime. However, the C–N–O angles were set at 120° and the angle between the plane of the phenyl ring and the plane of the oxime group was varied to find the minimum energy.

(2) For *syn*- and *anti*-acetaldoxime radicals, the bond lengths used were those for acetoxime as determined by Bierlein and Lingafelter.[15] The oxime carbon was assumed to be sp^2, and all bond angles were taken as 120°. Variation of the angles around this carbon produced little effect on the coupling constants. The C–N–O angle was varied to obtain the minimum energy.

(3) For the methylenimino radical, all bond angles were taken as 120°. The bond length was varied to obtain the minimum energy.

(4) For the formyl radical, C–H = 1.07 Å, C–O = 1.20 Å. The bond angle was varied to obtain the minimum energy.

(5) The benzonitrile radical anion has the same geometry as in ref 2.

(6) For the NH_2 radical, N–H = 1.07 Å, bond angle = 120°. The variation of geometry has no effect on the calculated N coupling constant for this radical.

(7) For the 2-pyridyl radical, C–N = 1.34 Å, C–C = 1.39 Å, C–H = 1.08 Å. This is the geometry of pyridine as reported by Bak.[16] The hydrogen on the 2-carbon (*ortho* carbon) has been removed.

(8) The pyridine cation has been assumed to have the same geometry as pyridine.

(9) For nitrogen(IV) oxide, N–O = 1.197 Å. The O–N–O angle equals 135°.

Results

The calculated and experimental hydrogen coupling constants are compared in Table I, while those for the nitrogen coupling constants are compared in Table II,

Table I. Comparison of Calculated and Observed Hydrogen Coupling Constants

Radical	Coupling constant Calcd	Exptl	Ref
Formyl (HCO)	67.1	136	17
Methylenimino (H_2CN)	90.0[a]	87.4	13
anti-Acetaldoxime (CH_3CHNO)			
CH_3	0.8	*b*	6
H	3.0	5.2	
syn-Acetaldoxime (CH_3CHNO)			
CH_3	0.1	*c*	6
H	17.1		
anti-Benzaldoxime (90° conformer, C_6H_5CHNO)			
ortho	2.0	1.4	*f*
meta	1.6	*b*	
para	3.5[d]	*b*	
H	3.9	6.2	
syn-Benzaldoxime (0° conformer, C_6H_5CHNO)			
ortho	0.8	*b*	*f*
meta	0.3	*b*	
para	0.3	*b*	
H	19.4	26.9	
2-Pyridyl (C_5H_4N)			
3-H	5.3		
4-H	9.3 } 7.4	4.3[d]	16
5-H	7.6		
6-H	0.0		
Pyridine cation[e]			
ortho H	27.0		
meta H	9.7		16
para H	38.8		

[a] Bond length 1.11 Å. [b] Splitting too small to be resolved. [c] Molecule too unstable to be observed, but coupling constants are expected to approximate those in the corresponding benzaldoxime. [d] See text for explanation of this apparent discrepancy. [e] This calculation was carried out to support a claim that this spectrum was incorrectly assigned. [f] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.*, 86 (1966).

Table II. Comparison of Calculated and Observed Nitrogen Coupling Constants

Radical	Calcd	Exptl	Ref
Methylenimino	11.4	11.4[a]	13
syn-Benzaldoxime	29.2	29.2[b]	*i*
anti-Benzaldoxime	29.4	31.6	*i*
syn-Acetaldoxime	31.9	*c*	
anti-Acetaldoxime	33.7	32.5	6
2-Pyridyl	33.8	29.7	*j*
Pyridine cation	52.5	*d*	
Benzonitrile anion	3.8	2.15	*k*
NH_2	12.0	10.1	*l*
		11.9[e]	*l*
NO_2	60.4	53.1[f]	*m*
		47.1[g]	*n*
		52.3[h]	*o*

[a] Used to calculate B in eq 2. [b] Used to calculate A in eq 2. [c] Not observed. [d] Experimental value uncertain. [e] ND_2 radical [f] Solid Ne matrix. [g] Gas phase. [h] Microwave spectra. [i] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.*, 86 (1966). [j] J. Bower, J. A. McRae, and M. C. R. Symons, *Chem. Commun.*, 542 (1967). [k] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963). [l] S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, *Phys. Rev. Letters*, **1**, 91 (1958). [m] P. H. Kasai, W. Weltner, Jr., and E. B. Whipple, *J. Chem. Phys.*, **42**, 1120 (1965). [n] J. G. Castle and R. Beringer, *Phys. Rev.*, **80**, 114 (1950). [o] A. Carrington and A. D. McLachlan in "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 143.

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Table III. Comparison of Planar and 90° Conformers of *syn*- and *anti*-Benzaldoxime

Radical	Nonbonded interatomic distances, Å Oxime O–*o*-H	 Oxime O–*o*-C	E_{total}, kcal/mole	A_{H}, Calcd	*G*, Exptl
Planar *anti*-benzaldoxime	1.86	2.61	−18,990.5	2.1[a] 9.8[b]	6.2[a] 1.4[b]
90° *anti*-Benzaldoxime	3.66	3.60	−19,007.9	3.9[a] 2.1[b]	6.2[a] 1.4[b]
Planar *syn*-benzaldoxime	3.93	4.27	−19,029.4	19.4[a] 0.8[b]	26.9[a] *c*
90° *syn*-benzaldoxime	4.49	4.59	−19,006.6	23.6[a] 0.2[b]	26.9[a] *c*

[a] Oxime hydrogen. [b] *ortho* ring hydrogen. [c] Coupling constant too small to be resolved.

The actual geometries of most of these radicals are unknown. Therefore, we were forced to determine the most stable configuration from the output of the extended Hückel calculation. All results listed are for the geometry which gave the lowest total energy.

For the radicals in which the geometry was varied in order to find an energy minimum the following results were obtained.

For the HCO radical, a bond angle of 120° gave the most stable radical.

For the H_2CN radical, a C–N bond length of 1.11 Å gave the most stable radical although this was a very shallow minimum.

For oximes (*syn*- and *anti*-acetaldoxime), calculations were carried out with CNO bond angles of 110, 115, 118, 120, 122, 125, and 140°. The EHT energy for both isomers proved to be most stable at 120°. In view of the above, the CNO angle was fixed at 120° in the benzaldoxime calculations and was not varied in order to save computer time. However, in benzaldoxime the angle between the plane of the phenyl ring and the plane of the CHNO group was varied. The results show that *anti*-benzaldoxime is 17.4 kcal/mole more stable when the two planes are perpendicular (90° conformer) than when the molecule is completely planar (0° conformer). On the other hand, the *syn* isomer is 22.8 kcal/mole more stable in the planar, conjugated form than in the 90° conformer. These conclusions are supported by comparing the calculated coupling constants for the various isomers with the experimental results.

The results of the calculations on *syn*- and *anti*-benzaldoxime as a function of the dihedral angle between the ring and CNO planes are contained in Table III. Also contained in this table are the distances of closest approach between atoms of the oxime group and atoms of the phenyl ring, namely the oxime oxygen distance from the *o*-H and *o*-C of the phenyl ring. We believe these data support the conclusions drawn above; *i.e.*, steric repulsion is important only in planar *anti*-benzaldoxime.

Discussion

The values for the observed and calculated hydrogen coupling constants are reported in Table I. The scaling factor used to convert spin density to coupling constant is that previously reported for a series of hydrocarbons.[2,3] The agreement between experimental and calculated is excellent in most cases. The transferability of this scaling factor to radicals containing oxygen and nitrogen is encouraging and suggests that the extended Hückel approximations are still yielding reasonably good wave functions. It is gratifying that when the experimental coupling constant is not observed, presumably due to its small value (footnote *b* of Table I), we calculate a very low value for it. This constitutes an experimental check on the theory.

Our calculated value for the formyl radical is in very poor agreement with experiment, but not much different from values calculated by other workers.[4,5] Cochran, *et al.*,[17] have suggested that the large coupling constant for this radical results from the admixture of a low-lying excited state by configuration interaction. If this is true, it explains the poor agreement of our calculated value, since our calculation does not include configuration interaction.

The unfortunately large value (3.5) calculated for the *p*-phenyl coupling constant of *anti*-benzaldoxime (Table I) is not unexpected in view of the inability of this method to calculate the *para* coupling constant of the phenyl radical.[2,4] This problem has been solved by Atherton and Hinchliffe[5] using the unrestricted Hartree–Fock (UHF) method with CNDO/2 integral approximations. While this UHF method gives better results for the phenyl radical, it does not give as good results as our method when all of the hydrocarbon radicals reported are considered.

It should be noted that our value of 120° for the CNO angle of the oximes does not agree with the value of 140° reported by Symons[18] for dimethylglyoxime. A calculation for *anti*-acetaldoxime with a CNO angle of 140° gives a coupling constant of 15.6 G compared to the experimental value of 5.2 G. This is much worse than the calculated value with a CNO angle of 120° reported in Table I. The reason for this discrepancy can be understood when we consider that the 140° value reported by Symons is obtained from a p/s ratio calculated from observed nitrogen anisotropic and isotropic hyperfine splittings. Thus, it is an approximate measure of p and s character of the nitrogen only for the MO containing the unpaired electron. The p and s character of any *one* MO does not uniquely establish the geometry about the atom. Thus Symons' analysis is not rigorously accurate. Our calculation, however, considers all the filled MO's in calculating the energy of the molecule, and hence we feel that it is more likely to predict the proper geometry.

It should be pointed out that when an angle of 125° is used in the *anti*-acetaldoxime, for example, the A_{N} and A_{H} values are 31.0 and 4.5, respectively, in better agreement with experiment, though the energy is not a minimum. Our calculations of the energy and the *A*

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values are not accurate enough to distinguish between 120 and 125°. To be consistent we have reported all values at minimum energy, even though there is uncertainty in the energies calculated by this procedure. However, the proton and nitrogen hyperfine coupling constants constitute a check on the geometry of the radical, and a reasonable fit of both is obtained at the minimum energy geometry for all radicals studied.

The large differences in the stability of the planar conformers of benzaldoxime is at first surprising. However, examination of molecular models shows that in the *anti* isomer there is a good deal of steric interference between the oxygen and the *o*-H and *o*-C. Table III describes the situation. Here we can see that only in the *anti*-planar configuration is the oxygen close enough to be repelled from the *ortho* ring position. Also note that the energies of the two 90° conformers are nearly equal, as would be expected since the oxygen in these conformers is far away from everything else. Also, in the solid state the crystal structures of Jerslev[14] show the *syn* isomer to be planar, but the *anti* isomer shows an angle of 19° between the two planes. The calculated coupling constants are very sensitive to the geometries and are in excellent agreement with the conclusions drawn above on the basis of the energies. The unstable geometries give very poor fits with the experimental coupling constants.

There is a controversy concerning the assignment of the spectra of the *syn* and *anti* isomers of the oximes which these calculations help to resolve. Rassat, *et al.*,[7] assigns the larger coupling constant ($\sim$25 G) to the *syn* isomer, while the smaller ($\sim$5 G) coupling constant is assigned to the *anti* isomer. Thomas[6] has made the opposite assignment. Berthier, *et al.*,[19] have supported their assignment with an MO calculation on formaldoxime, a radical which has not been observed experimentally. Their calculated results were 43.2 G for the *cis* proton and 11.7 G for the *trans* proton, both of which are too large. We feel that this error is caused by their use of 134°, the bond angle of NO_2, for the CNO bond angle. One would expect the CNO angle to be somewhat less than the value in NO_2, and this is supported by our calculations which show a minimum energy at 120°. Since the hydrogen coupling constants for the radicals which we have calculated rapidly increase with CNO angle, we feel that this is the source of the error in the calculations of Berthier, *et al.* Hence our calculations confirm that the correct assignment is that of Rassat. Since about 20% of the unpaired electron spin density of the oximes is in the "lone-pair" orbital of N, these radicals can be viewed as analogous to the vinyl radical in that the largest coupling occurs with the proton opposite the nonbonding orbital containing the unpaired electron.

The most surprising and rewarding part of this work has been our success in calculating nitrogen coupling constants. The method seems to be successful with the π radicals benzonitrile and NH_2 as well as for the σ radicals reported. The value for NO_2 is a little high but is close to that reported by McLachlan, *et al.*[4] (74 G), who used a less empirical approach than ours to calculate the nitrogen hyperfine coupling. We believe that the value of 107 G for the N hyperfine coupling measured by Bird, *et al.*,[20] in CCl_4 solution must be in error, in view of the other reported values and our calculated results.

The theoretical value for *A* in eq 2 can be calculated for a nitrogen atom from the equation

$$A\,(\mathrm{G}) = \frac{8\pi g\beta g_N\beta_N}{3\gamma_e h}\psi(0)^2$$

where g and g_N are the g values for the electron and the nitrogen nucleus, β and β_N are the Bohr and nuclear magnetons, and $\psi(0)$ is the value of the N_{2s} orbital at the nitrogen nucleus. Evaluation of *A* using a Clementi analytical SCF function[21] gave a value of 548.2 G, which does not agree at all with our empirical value of 1425 G. This could be explained if the N_{1s} orbital makes a large contribution to the nitrogen hyperfine splitting either directly or *via* spin polarization. Our empirical method would incorporate this contribution in the 2s orbital and cause the scaling factor to be larger than 548. However, we do not feel that the 1s contribution is large enough to account for the observed discrepancy. It is more reasonable to suppose that our wave functions are in error, requiring a large value for *A* in order to calculate the proper coupling constant. Though internal consistency suggests that the relative changes in the wave functions are good for this series of compounds, the absolute values may not be accurate. This does not present a serious problem since the applications made here only require that the calculation give consistent results from molecule to molecule. From these results, it would appear that this condition is satisfied but we do not have great accuracy in any given wave function.

The value for *B* in eq 2 is approximately what would be expected by comparison with similar values for ^{13}C splitting of π systems. Also, the sign of *B* should be positive, as for ^{13}C, because spin polarization of the s electrons by the p electrons leaves positive spin at the nucleus. McLachlan[22] adds yet another term to his ^{13}C equation due to the spin density on adjacent atoms. However, this term would be small ($\sim$4 G for a single electron on an adjacent atom), and our failure to include this term introduces only a small error in our work.

Berthier, *et al.*,[19], were able to calculate a very accurate value for the nitrogen hyperfine coupling constant of formaldoxime using a value of 550 for *A* and 59.3 for *B*. However, this would give splittings which are much too large for all our π radicals. For example, it would predict about 15 G for benzonitrile radical anion and 59.3 G for NH_2, both of which are clearly much too high.

Another application of these calculations to the experimental assignment of spectra is illustrated by the 2-pyridyl radical calculation. Earlier work[23] had assigned the epr spectra of γ-irradiated pyridine to the pyridine cation. However, our results indicate that this is unlikely since the agreement between the observed spectra and that calculated for the pyridine cation is very bad. Conversely, if the radical obtained is the

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2-pyridyl radical, as suggested by Symons,[24] then the agreement for both the N and H hyperfine coupling constants is much better. The observed spectrum shows three protons with a coupling constant of 4.3 G[23] and a nitrogen coupling constant of 29.7 G.[19] Examination of the calculated proton coupling constants for the pyridine cation, shown in Table I, reveals no correlation of the calculated and observed spectra. Further, the calculated nitrogen coupling constant for the cation is 52.5 G, which also does not agree with the observed 30 G. However, when we consider the 2-pyridyl calculation, the agreement of the nitrogen coupling constant is much better. Also, when we consider our failure to calculate the coupling constant of the *para* proton of the phenyl radical, we reach the conclusion that our value for the 5-H coupling constant should be about 2–4 G. Using this value, a reproduction of our calculated spectra for the 2-pyridyl radical agrees well with the spectrum observed by Tsuji, *et al.*,[23] since many of the lines due to proton coupling are calculated to be so close that they would not be resolved. Hence we conclude that the radical obtained on irradiation of pyridine is the 2-pyridyl radical as suggested by Symons,[24] rather than the pyridine cation.

The extended Hückel method seems to give surprisingly good results when applied to the calculation of epr hyperfine coupling constants, and the range of the applicability seems large. It appears to be a useful tool in the difficult task of determining the structure of radicals. Trends in the wave functions appear to be significant but their absolute magnitudes do not. The neglect of spin polarization sets a limit on the accuracy with which we can calculate spin densities, and we have taken this into consideration in the conclusions we have drawn. We do not ordinarily know from experiment the sign of the coupling constant; we cannot calculate a negative spin density, and in some cases where we calculate a small value for A this could turn out to be negative. We are currently attempting to improve the calculation by including spin polarization. Preliminary results indicate spin polarization is very important for protons bonded to atoms containing a large fraction of the unpaired spin density.[25] For example, the α-proton coupling constant in the vinyl radical is probably negative. Consequently, we can draw no conclusions[2,3] that depend on the magnitude of a coupling constant directly bonded to a carbon atom containing most of the unpaired spin density.

The success in calculating nitrogen hyperfine coupling constants suggests that this is not as difficult a problem as one might suppose. Further, this method can possibly be extended to calculate ^{13}C and ^{19}F hyperfine splittings.

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Studies of Some Binuclear, Oxygen-Bridged Complexes of Iron(III). New Iron(III)–2,2′,2″-Terpyridine Complexes

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Abstract: Three complexes of iron(III) with the tridentate ligand 2,2,′2″-terpyridine have been isolated and characterized. One is a simple, high-spin octahedral complex, $[Fe(terpy)Cl_3]$, while another, $[Fe(terpy)_2](ClO_4)_3$, is a low-spin octahedral complex. The third, $[Fe_2(terpy)_2O](NO_3)_4\cdot H_2O$, is a binuclear complex exhibiting properties similar to those of the related 1,10-phenanthroline, 2,2′-bipyridine, and N,N′-ethylenebis(salicylideneiminate) binuclear species. The magnetic behavior and the Mössbauer, electronic, and infrared spectra of the binuclear terpyridine complex are reported and compared with those of other similar systems. The possibility of a quartet ($S = {}^3/_2$) *vs.* a sextet ($S = {}^5/_2$) spin state for the iron is discussed.

Complexes of Fe(II) with 2,2′,2″-terpyridine (hereafter terpyridine or terpy) having one or two terpyridines per iron are known. The mono complexes having the general formula $[Fe(terpy)X_2]$ ($X^- = Br^-, SCN^-, I^-$) have been shown on the basis of X-ray, magnetic, and spectroscopic studies[2,3] to have a distorted square-pyramidal structure. The bis complexes are low spin and have a distorted octahedral configuration. Mössbauer spectra of the bis complexes show an unusually large (for low-spin Fe(II)) quadrupole splitting (ΔE_q)[3,4] similar to that observed for the $[Fe(CN)_5NO]^{2-}$ ion.[5] The generally accepted explanation for the large values of ΔE_q observed for these systems is that there exists considerable anisotropic covalent bonding involving the t_{2g} orbitals. In the

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