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Use of the EPR Half-Field Transition To Determine the Interspin Distance and the Orientation of the Interspin Vector in Systems with Two Unpaired Electrons

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Abstract: For systems containing two unpaired electrons with g values near 2 and an interspin distance of r, the intensity of the forbidden half-field transition is proportional to r^{-6}. The hyperfine splitting of the half-field signal is dependent on the relative orientations of the nuclear hyperfine tensors for the two electrons and the orientation of the interspin vector. Thus the value of r and the relative orientations of the hyperfine tensors can be determined independently and independent of the value of the exchange coupling constant J. The method has been calibrated with seven molecules which have well-characterized geometries: a copper dimer, four dinitroxyl radicals, and two spin-labeled copper complexes. The absolute value of J for these molecules ranged from 25×10^{-4} to about 100 cm^{-1}. Two three-spin systems have been examined. The method has also been applied to a spin-labeled copper complex for which the copper–nitroxyl distance could not have been obtained by other EPR methods.

Introduction

Systems containing two unpaired electrons are important in areas of chemistry as diverse as radical pairs in photosynthetic bacteria,[1] spin-labeled metalloenzymes,[2] metal–metal dimers,[3] and organic diradicals.[4] In each case there is interest in determining the distance between the two electrons. It is also of interest to determine the orientation of the interspin vector relative to other anisotropic tensors of the individual electrons such as nuclear hyperfine tensor(s).

Two methods have commonly been used to determine the distance, r, between two unpaired electrons from EPR powder spectra. (a) The position of the low-field edge of the half-field signal in a powder spectrum is given by eq 1 where ν is the

$$H_{\min}(\Delta M_s=2) = \frac{1}{2g\beta}\left[(h\nu)^2 - 4\left(\frac{D^2}{3} + E^2\right)\right]^{1/2} \qquad (1)$$

spectrometer operating frequency and D and E are the zero-field splitting parameters.[4-6] If it is assumed that E is negligible, then the shift between the low-field edge of the half-field signal ($H_{\min}(\Delta M_s=2)$) and that calculated from $h\nu/2g\beta$ (in eq 1) is a measure of D. If it is assumed that D is due only to dipolar interaction with no contribution from anisotropic exchange, the value of D obtained from eq 1 can be used in eq 2 to calculate

$$D = 3g^2\beta^2/2r^3 \qquad (2)$$

D is in ergs and r is in cm

$$D = 3g\beta/2r^3 = 1.39 \times 10^4\ (g/r^3) \qquad (3)$$

D is in gauss and r is in Ångströms

a value of r. When r is greater than about 5 Å, the shift in the half-field transition becomes negligibly small so the use of this equation is limited to short interspin distances. (b) The separation $2D$ between the low-field and high-field turning points in frozen glass or powder EPR spectra has been used to obtain r.[7] In this case it is convenient to express D in gauss as in eq 3. This method does not give accurate results when the dipolar coupling is of the order of magnitude of nuclear hyperfine couplings or the exchange interaction.[8]

Three less widely used methods have been proposed for the determination of r in dinitroxyls. Russian workers have used peak-height ratios in frozen glass spectra and changes in the second moments of frozen glass spectra to determine values of r in the range of 12 to 22 Å.[9,10] Rassat et al. have used the temperature dependence of line widths to estimate values of r.[11] However, when J is of the same order of magnitude as the dipolar coupling, the splittings of the EPR transitions have contributions from both the exchange and dipolar terms. These methods determine only the total splittings and do not provide a means to separate the two contributions to the electron–electron interaction.

We recently reported a perturbation calculation of the EPR spectra of spin-labeled copper complexes in frozen solution.[12] The use of the same calculational approach showed that the ratio of the intensity of the forbidden half-field transition ($\Delta M_s = 2$) to the intensity of the allowed transitions ($\Delta M_s = 1$) was dependent on the value of r, and independent of the value of the exchange coupling constant J. We have therefore obtained experimental data for the intensities of the transitions in compounds I–X (Chart I). Compounds I–VII were selected for study because their geometries were well defined by other techniques and the structures were expected to be relatively rigid. Compounds VIII and IX were of interest because they contain three unpaired spins. Compound X was chosen as an example of a molecule for which the half-field transition could be used to determine the interspin distance although other methods of determining r were not applicable. Preliminary results of this study have been reported.[8]

Experimental Section

The compounds used in this study were prepared by literature methods: I,[13] II,[14] III,[15] IV,[16] V,[17] VI,[18] VII,[18] VIII,[19] IX,[19] X.[20]

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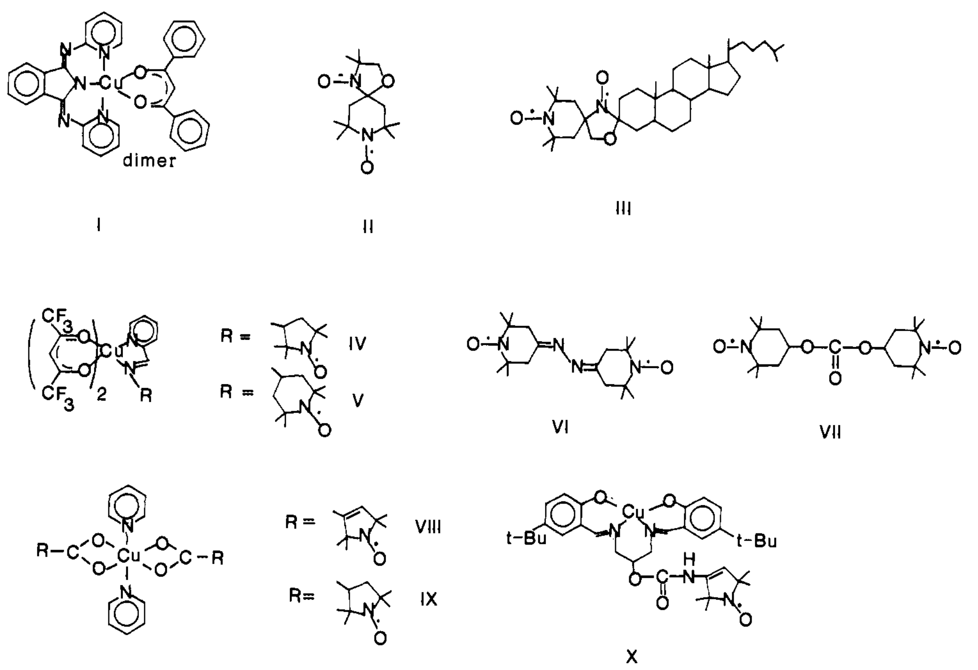
Chart I



X-band EPR spectra were obtained on a Varian E-9 operating between 9.100 and 9.105 GHz. Q-band spectra were obtained on the spectrometer which has been described previously.[21] X-band and Q-band spectra were collected as 1000 point arrays in a Varian 620/L103 minicomputer. Background spectra of the cavity and sample tube were subtracted prior to integration of the spectra of the half-field transition. S-band spectra were obtained at the National Biomedical ESR Center in Milwaukee and manipulated using a PDP 11/34 minicomputer. EPR spectra of I were obtained on a powdered sample at room temperature. Spectra of samples II to XI were obtained on frozen toluene or 4:1 toluene/tetrahydrofuran glasses at −180 °C in 4-mm quartz tubes.

Computer Simulations

Computer simulations were obtained with the computer program MENO which has been used to simulate frozen-solution EPR spectra of spin-labeled copper complexes.[12] A similar approach was used in the analysis of single-crystal EPR spectra of spin-labeled copper complexes.[22] The Hamiltonian (eq 4) consists

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{int}} \qquad (4)$$

of terms for independent electrons 1 and 2 as given in eq 5 and

$$\mathcal{H}_i = \sum_{j=x_i,y_i,z_i} (\beta g_j S_{ij} H_j + A_j S_{ij} I_{ij}) \qquad i = 1,2 \qquad (5)$$

an interaction term as given in eq 6. The interaction term includes

$$\mathcal{H}_{\text{int}} = -J S_1 S_2 + \mathcal{H}_{\text{dipolar}} \qquad (6)$$

an isotropic exchange contribution and an anisotropic dipolar contribution. The symbols in eq 4–6 have their usual meanings and are discussed in detail in ref 3, 12, 22, and 23. The perturbation calculations were carried to second order. The splitting between the singlet and triplet levels is J, and a negative value of J indicates an antiferromagnetic interaction. The angles which define the relative orientations of the nuclear hyperfine axes of electrons 1 and 2, and the dipolar tensor, are shown in Figure 1. In the following discussion r is used to denote the magnitude of the interspin vector and its orientation is defined by the angles ϵ and η.

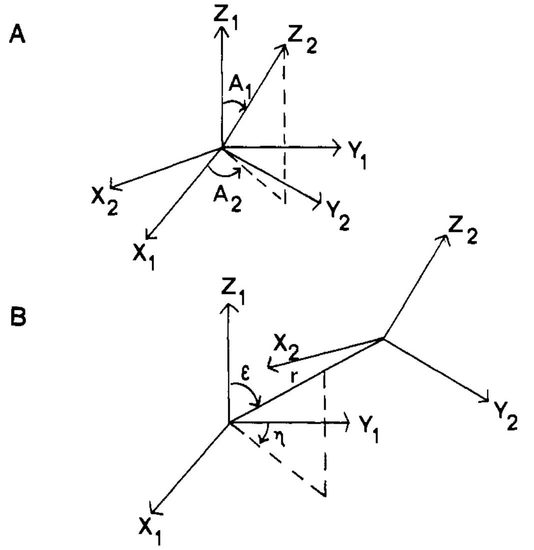


Figure 1. Definitions of the orientation parameters. The orientation of the z axis of electron 2 relative to the axes of electron 1 is given by angles A_1 and A_2. The orientation of the z axis of the dipole tensor relative to the axes of electron 1 is given by angles ϵ and η. Throughout the text r is used to denote the distance between the two unpaired electrons.

Results and Discussion

The interaction between two unpaired electrons will in general have an isotropic exchange contribution and an anisotropic dipolar contribution. To obtain the distance between the two spins it is necessary to separate the effects of the two terms. In describing the interaction it is convenient to use wave functions that are written in terms of the total spin quantum numbers for the two electrons (M_s). To first approximation the effect of exchange is to cause an energy separation between the singlet and triplet $M_s = 0$ energy levels. The dipolar interaction, D, shifts the energy of the triplet $M_s = \pm1$ levels relative to the triplet $M_s = 0$ level.[24]

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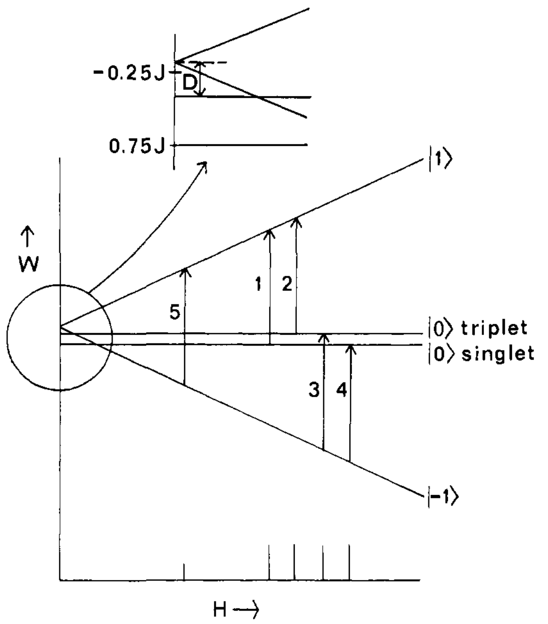


Figure 2. Energy level diagram for two interacting spins when the magnetic field is along the z axis of the dipole tensor. The Hamiltonian for the interaction is given in eq 5. The diagram is drawn for $J < 0$.

The resulting energy level diagram is shown in Figure 2. The $\Delta M_s = 1$ transitions are labeled as transitions 1 to 4. Unless the value of J is so large that only the transitions within the triplet manifold are observed (transitions 2 and 3), the appearance of the EPR spectrum will depend on the values of both J and r. However, to first order, the energy for transition 5, the forbidden $\Delta M_s = 2$ transition, is independent of the values of both J and r. For interspin distances greater than about 5 Å the second-order effects on the energy of transition 5 are negligible and the position of the half-field transition contains no information about J or r. Therefore, although the observation of a half-field signal has been used to indicate the presence of electron–electron spin–spin interaction, it has not been used widely to characterize the interaction. Our calculations indicated that for two $S = {}^1/_2$ centers with g values near 2 and $r > 4.5$ Å, the integrated intensity of the half-field signal was determined only by the interspin distance, r, and that the hyperfine splitting of the half-field signal was determined only by the relative orientations of the nuclear hyperfine tensors of the two unpaired electrons and the orientation of the interspin vector relative to the nuclear hyperfine tensors. Thus the values of r and the orientation parameters can be determined independently by analysis of the half-field signal.

Intensity of the Half-Field Signal in Randomly Oriented Samples. It is convenient to relate the integrated intensity of the half-field transition (Figure 2, transition 5) to the integrated intensity of the allowed transitions (Figure 2, transitions 1 to 4) for the same sample (eq 7). The use of the ratio of intensities for two portions

$$\text{relative intensity} = \frac{\text{intensity of } \Delta M_s = 2}{\text{total intensity of } \Delta M_s = 1} \tag{7}$$

of the spectrum of one sample eliminates the need for many of the correction factors which would otherwise be required for accurate intensity determinations.[25,26] Calculations at S-band, X-band, and Q-band indicated that the relative intensity could be expressed as in eq 8 where ν is the spectrometer operating frequency in GHz and A was 19.5 for organic diradicals with $g = 2.006$, and A was 21 ± 2 for spin-labeled copper complexes. Since the relative intensity depends on r^{-6}, there is less uncertainty in the value of r obtained from eq 8 than the uncertainty in the value of the coefficient A.

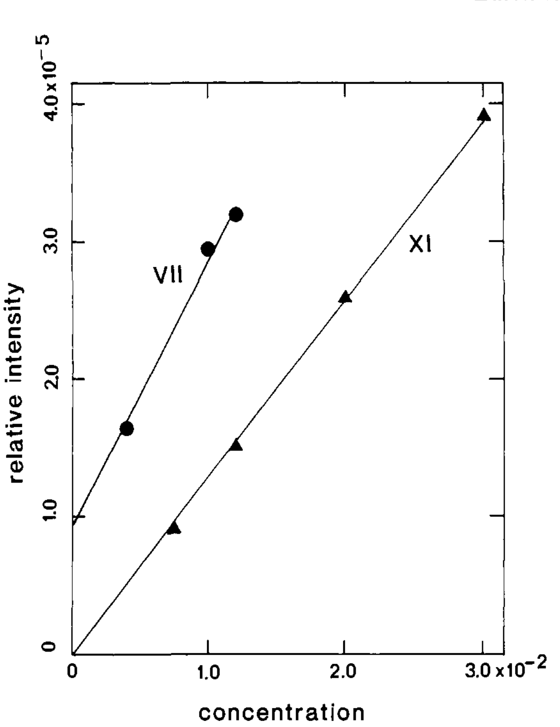
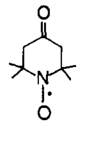


Figure 3. Relative intensities of the half-field transitions in monoradical XI (▲) and diradical VII (●) as a function of the molar concentration in 4:1 toluene/THF glasses at −180 °C.

$$\text{relative intensity} = \frac{A}{r^6}\left(\frac{9.1}{\nu}\right)^2 \tag{8}$$

The dependence of the relative intensity on r^{-6} is obtained whether the spin–spin interaction is inter- or intramolecular. For molecules with short interspin distances in dilute solution, the contribution to the relative intensity of the half-field transition from intermolecular interactions is negligible. For molecules with longer interspin distances, the relative intensity of the half-field transition includes contributions from both inter- and intramolecular spin–spin interactions. When the interaction is intramolecular, both the numerator and denominator of eq 7 are proportional to the concentration of the solution so the ratio is independent of concentration. When the interaction is intermolecular, the number of molecules with short interspin distances (and therefore the intensity of the half-field transition) is dependent on the square of the concentration. The intensity of the allowed transitions is still proportional to concentration so the ratio of the intensities of the forbidden and allowed transitions (eq 7) is proportional to concentration. The same conclusion can be reached by using a shell model of the solute distribution and integrating the effect of spin–spin interaction over a distribution of values of r. Since the intermolecular contribution is concentration dependent and the intramolecular contribution is concentration independent, the intramolecular component can be obtained by plotting the relative intensity of the half-field transition as a function of concentration and extrapolating to infinite dilution. To test the validity of this approach the relative intensity of the half-field transition was obtained for monoradical XI in frozen



XI

toluene glasses. No intramolecular interactions would be expected for XI. Spectra were obtained at 3.0×10^{-2}, 2.0×10^{-2}, 1.2×10^{-2}, and 7.5×10^{-3} M. Linear extrapolation to infinite dilution

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(24) In ref 8 the phrase "exchange causes mixing of the singlet and triplet $M_s = 0$ levels" should have read "exchange causes mixing of the spin functions of the two electrons and changes the relative energies of the singlet and triplet $M_s = 0$ levels."

(25) Eaton, G. R.; Eaton, S. S. *Bull. Magn. Reson.* **1980**, *1*, 130–138.

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gave a relative intensity of 0 as shown in Figure 3. For dinitroxyl VII extrapolation of the relative intensity to infinite dilution gave a nonzero value (Figure 3).

Two characteristics of the half-field transition make signal detection easier than might be expected on the basis of the values of the relative intensity. The variation of the energy of the half-field transition as a function of the orientation of the molecule in the magnetic field is less than for the allowed transitions so the total intensity of the half-field signal is spread over a relatively narrow range of magnetic fields. Secondly, the saturation behavior of the half-field signal is markedly different from that of the allowed transitions. Since the half-field transitions have small transition probabilities, it is harder to perturb the relative populations of the energy levels involved in the transition than would be expected for an allowed transition. Therefore, it is possible to use a much higher microwave power for the forbidden transitions than for the allowed transitions. The −180 °C spectra of the allowed transitions had to be taken at microwave powers between 0.1 and 0.4 mW, depending on the sample, to avoid saturation. Spectra of the half-field transitions in dinitroxyls II and III showed slight saturation at 200 mW, but the spectra of the half-field signals for the other samples showed no evidence of saturation at 200 mW. Other papers have also reported that the forbidden transitions in triplet systems do not saturate readily.[27–30]

When J is large relative to kT, there is a significant temperature dependence of the populations of the singlet and triplet energy levels. However, when J is this large the only allowed transitions are within the triplet manifold, and the transitions between the singlet and triplet levels have negligible intensity. Thus the effect of changing the temperature has the same impact on the intensity of the allowed and half-field signals and causes no difficulties in the use of the relative intensity to obtain the interspin distance.

To use eq 1, 2, 3, or 8 to determine the value of r from the EPR spectra of a two-spin system, it is necessary to assume that anisotropic exchange is negligible. The extent to which this assumption is valid depends both on the magnitude of J and on the anisotropy of the g values.[31] In organic diradicals the g values are nearly isotropic so anisotropic exchange is likely to be negligible even for relatively large values of J. For the copper complexes examined in this study the values of J are sufficiently small that anisotropic exchange is probably not significant. However, more studies are required to determine how large J and/or the g value anisotropy can be without causing errors when eq 1, 2, 3, or 8 are used. Since eq 8 is most likely to be useful at longer values of r, the likelihood of interference from anisotropic exchange is less than for eq 1.

These results prompted us to search the literature to see what information was available concerning the intensity of the half-field transition. Both Pake and Slichter, in their classic texts, noted that dipolar interaction between two spins led to a transition at half-field with intensity proportional to $(1/r^3H_0)^2$.[32,33] In 1969 Iwasaki et al. used the value of D obtained from the allowed transitions in an irradiated polymer to obtain a value of r and then used eq 9 with $B = 8/15$ to estimate the concentration of radical

$$\text{relative intensity} = B\,(d_\perp/H)^2 \qquad (9)$$

H is the resonant field for the allowed transitions

pairs.[34] Subsequent reports have used various forms of eq 9 to determine the concentration of radical pairs in irradiated samples.[35–37] Glarum and Marshall independently derived eq 9 with $B = 4/15$ and used it in a study of radical-pair formation by nitroxyl radicals in the plastic phase of camphene.[38] In comparing eq 9 with the equations in ref 34–38, it must be noted that in ref 34, 35, and 37 the intensity of the half-field transition was compared with the intensity of one of the allowed transitions, but in ref 36, 38, and the present report the total intensity of the allowed transitions was used. Since $d_\perp = D$, substitution of eq 3 into eq 9 with $B = 4/15$, $g = 2.00$, and $H = 3250$ gives eq 8 with $A = 19.5$ and $\nu = 9.10$ GHz. Thus the use of $B = 4/15$ is in good agreement with our results. In his general paper on the treatment of spin Hamiltonians Iwasaki's expression for transition probability[39] does not include the $1/g$ correction for field-swept spectra that was first recognized by Aasa and Vanngard the following year.[40a] Inclusion of this correction factor reduces his value of $B = 8/15$ used in ref 34–37 to $B = 4/15$[40b] which is in good agreement with our results. In 1974 Dubinskii et al. used Iwasaki's results[34] (eq 9 with $B = 8/15$) to obtain eq 10.[41] They examined

$$\text{relative intensity} = 38/r^6 \qquad (10)$$

several dinitroxyls with r in the range of 9 to 12 Å and reported good agreement between the values of r obtained from eq 10 and values of r obtained by other methods.[41] Despite these results there is a recent report in the literature that the intensity of the half-field transition depends on r^{-3}.[42]

Although there is ample indication in the literature that the intensity of the half-field transition depends on r^{-6}, there has been some disagreement over the coefficient in the relationship, and this dependence has been used only in one report to determine interspin distances. The results reported in this paper provide the first calibration with a variety of molecules and a wide range of values of r. Now that EPR spectrometers are routinely computer interfaced, it is straightforward to obtain integrated intensity data and the use of eq 8 looks promising.

Hyperfine Splitting of the Half-Field Signal for Randomly Oriented Samples. Kurita showed that in a single crystal the orientation dependence of the relative intensity of the half-field transition is given by eq 11 with $C = 1.0$:[43]

$$\text{relative intensity} = C\left(\frac{d_\perp \sin 2\theta}{H}\right)^2 \qquad (11)$$

where H is the resonant field for the allowed transitions and θ is the angle between the magnetic field and the z axis of the dipole tensor. In comparing eq 11 with the corresponding equations in the literature, it must be noted that in ref 34, 37, 43, and 44 the intensity of the half-field transition was compared with the intensity of one of the allowed transitions, but in ref 36, 45, and the present report the total intensity of the allowed transitions was used. Inclusion of the Aasa and Vanngard correction factor

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(44) Iwasaki, M.; Toriyama, K.; Muto, H.; Nunome, K. *J. Chem. Phys.* **1976**, *65*, 596–606. The coefficient in eq 13 of this paper should have been 1/4: M. Iwasaki, personal communication, April 1983.

(45) Toriyama, K.; Iwasaki, M. *J. Am. Chem. Soc.* **1979**, *101*, 2516–2523.

reduces the coefficient C in eq 11 to 0.5.[40] Since the intensity depends on $\sin^2 2\theta$, the transition probability is minimum when the magnetic field is along the principal axes of the dipole tensor and maximum at 45° away from the z axis. Thus the molecules for which the magnetic field is away from the principal axes of the dipole tensor dominate the spectra. The orientation dependence of the signal intensity has been verified experimentally in single crystals.[27,46-48]

When $r < 4.5$ Å, the splitting of the half-field transition is dominated by the value of D.[47] At larger values of r, D is negligible relative to $h\nu$, and the splitting is dominated by the nuclear hyperfine interaction at orientations of the molecule where the magnetic field is away from the axes of the dipole tensor. Thus the observed hyperfine splitting in a powder sample depends on the orientation of the dipole tensor relative to the nuclear hyperfine tensors.

To first order, the resonant fields for the allowed and forbidden transitions are given by eq 12 and 13, respectively:[12]

$$H_i = \frac{h\nu}{g\beta} \pm \frac{D_{zz}}{2g\beta} - \frac{\frac{1}{2}(K_1 m_1 + K_2 m_2)}{g\beta} \pm \frac{\phi}{g\beta} \qquad i = 1\text{–}4 \qquad (12)$$

$$H_5 = \frac{h\nu}{2g\beta} - \frac{\frac{1}{2}(K_1 m_1 + K_2 m_2)}{g\beta} \qquad (13)$$

where

$$\phi = [D_2^2 + D_6^2 + \tfrac{1}{4}[\beta H(g_1 - g_2) + (K_1 m_1 - K_2 m_2)]^2]^{1/2} \qquad (14)$$

D_{zz}, D_2, and D_6 are components of the spin–spin interaction matrix as described in ref 12 and 23, g is the average g value for the two electrons at a particular orientation in the magnetic field, and K_1, K_2 are the nuclear hyperfine couplings to electrons 1 and 2, respectively, at a particular orientation. As the spin–spin interaction goes to zero, the value of ϕ approaches $^1/_2[\beta H(g_1 - g_2) + (K_1 m_1 - K_2 m_2)]$ and the resonant fields for transitions 1–4 approach those of the independent electrons with hyperfine splittings K_1 and K_2. As the spin–spin interaction becomes large relative to differences in the g values and hyperfine couplings, the value of ϕ approaches $(D_2^2 + D_6^2)^{1/2}$, the transitions occur at the average of the g values for the two electrons, and the hyperfine splittings for transitions 1–4 are reduced to $K_1/2$ and $K_2/2$. Between the two limits the hyperfine splittings have intermediate values. The magnitude of the interaction required to reach the strong interaction limit depends on the g and a anisotropy of the system. Thus the hyperfine splitting observed for the allowed transitions is an indication of the magnitude of the spin–spin interaction. Since ϕ does not occur in the expression for the half-field transition (eq 13), the hyperfine splittings are $K_1/2$ and $K_2/2$ independent of the magnitude of the spin–spin interaction. Most studies reported in the literature have examined systems in which the spin–spin interaction was sufficiently strong that the hyperfine splitting of the allowed transitions was half that expected for the independent electrons and so the splittings of the allowed and forbidden transitions were identical. The fact that this is not always true has not been pointed out. Iwasaki et al. noted that the hyperfine splittings for both the $\Delta M_s = 1$ and $\Delta M_s = 2$ transitions in radical pairs were half those observed for the monoradicals, but did not note that this was true only because the spin–spin interaction was strong.[34] Grivet implied that the hyperfine splitting was always the same for the two transitions.[27] Parmon et al. erroneously stated that the observation of a five-line pattern for the half-field signal of a dinitroxide showed that J was large.[49] The half-field spectrum for dinitroxyl VII which is discussed below is an example of a five-line spectrum that is observed even when J is small. In a recent paper, Iwasaki et al. stated incorrectly that the observation of hyperfine splitting on the half-field transition that was half that expected for the isolated radicals was characteristic of spin exchange coupled pairs.[45]

Table I. Comparison of the Values of r^a Obtained from the Relative Intensity of the Half-Field Transition and Values Obtained by Other Methods

compound	r from eq 8	r from eq 3^b	r from other methods^c
I	4.48	4.1 (13)	4.453 (13)
II	4.94	5.02 5.05 (14)	
III	4.94	4.90 5.02 (15)	
IV	5.7		5, 7 5.4 (51)
V	6.9		6.5, 8 ~6.5 (52–54)
VI	8.6		9.0 8.2 (55) 9.0–9.3 (11)
VII	11.3		11 11.2 (57) 11.58 (56)

^{a} Values are given in angströms. ^{b} Using the value of D obtained from the splitting of the allowed transitions. Values taken from the literature are indicated by the reference number in parentheses following the value of r. ^{c} Values taken from the literature are indicated by the reference number in parentheses following the value of r. The methods used are discussed in the text.

Because the splitting of the half-field signal (for $r > 4.5$ Å) is independent of the values of r and J, it is possible to obtain orientation information from the splitting of the half-field signal without complications from the values of r and J. The same information is present in the allowed transitions, but to obtain the information by simulation of the allowed spectra it is necessary to vary the values of both r and J as well as the orientation parameters.

Calibration with Molecules of Known Geometry. To determine the accuracy with which the values of r and the orientation parameters could be obtained from the relative intensity of the half-field transition and the hyperfine splitting of the half-field transition, respectively, EPR spectra of compounds I to VII were examined. The results are summarized in the following paragraphs. The values of r are summarized in Table I. Intermolecular spin–spin interactions were negligible relative to intramolecular interactions for compounds II to V at concentrations up to 1×10^{-2} M. For compounds VI and VII the relative intensity of the half-field transition due to intramolecular interaction was obtained by extrapolation to infinite dilution.

An X-ray crystallographic study of copper complex I reported that the molecules pack uniquely in the crystal as dimers with a copper–copper distance of 4.453 Å.[13] The X-band EPR spectra of a powder sample of I is shown in Figure 1 of ref 13. It is difficult to obtain a value of D from the allowed transitions because of the presence of copper hyperfine splitting, but Addison et al. estimated a value of 0.042 cm^{-1} which corresponds to a value of 4.1 Å for r.[13] The spectra which we obtained on a sample of I provided by Professor Addison were in good agreement with the spectra reported in ref 13. The relative intensity of the half-field transition was 2.47×10^{-3}. Substitution into eq 8 gave $r = 4.48$ Å which is in excellent agreement with the X-ray results. The hyperfine splitting on the half-field transition was not sufficiently well resolved to obtain orientation information.

A single-crystal EPR study of dinitroxyl II doped into the analogous diamagnetic diamine found $D = 216$ G which corre-

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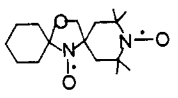
(47) Kottis, P.; Lefebvre, R. *J. Chem. Phys.* **1963**, *39*, 393–403.

(48) Karra, J. S.; Kemmerer, G. E. *Solid State Commun.* **1981**, *40*, 53–56. In this report the authors erroneously used linewidth × height instead of linewidth^2 × height to evaluate the area under a first derivative peak. The use of the correct expression makes the maximum in their intensity data fall closer to 45 than their figure indicates.

(49) Parmon, V. N.; Kokorin, A. I.; Zhidomirov, G. M. *Z. Strukt. Khim.* **1977**, *18*, 132–177 (pp 104–107 in translation).

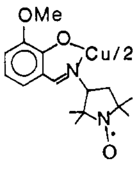
sponds to $r = 5.05$ Å (eq 3).[14] The EPR spectrum which we obtained at 90 K for the allowed transitions of II in 4:1 toluene/THF is in good agreement with that shown in Figure 6 of ref 14 for II in an EPA (diethyl ether/isopentane/ethanol, 5:5:2) glass at 77 K. The value of $2D$ from the frozen glass spectrum is 445 G which corresponds to $r = 5.02$ Å (eq 3). There was a small amount of monoradical present in the sample, but the peaks for the monoradical were well separated from the peaks for the diradical. Therefore, the double integral of the center portion of the spectrum (the monoradical signal) was subtracted from the double integral of the full spectrum to give the intensity of the allowed transitions. The relative intensity of the half-field transitions was 1.35×10^{-3} which corresponds to $r = 4.94$ Å (eq 8). The splitting of the half-field transition for II is similar to that for III which is discussed below.

The EPR spectrum of the allowed transitions for dinitroxyl III in an EPA glass is shown in Figure 1b of ref 15. The observed value of $2D$ of 455 G corresponds to $r = 5.02$ Å (eq 3). In a 4:1 toluene/THF glass we obtained a spectrum that is similar to the one in ref 15 but with $2D = 466$ G which corresponds to $r = 4.90$ Å. The intensity due to the monoradical impurity signal was subtracted from the total intensity of the allowed transitions to obtain the intensity of the allowed transitions in the diradical. The relative intensity of the half-field transition (1.34×10^{-3}) corresponds to $r = 4.94$ Å (eq 8) which is in excellent agreement with the values obtained from the allowed transitions. The EPR spectra of the allowed and forbidden transitions for II and III are similar to the spectra of the closely related diradical XII which are shown in Figures 2 and 5 of ref 50. Analysis of the temperature dependence of the intensity of the EPR spectrum of XII gave $|J| = 110\ \text{cm}^{-1}$.[50] The values of J for II and III are expected to be similar to that for XII. Michon and Rassat have shown that when J is large relative to the nitrogen hyperfine splitting and the dipolar splitting an analysis of the nitrogen hyperfine splitting of the allowed transitions when the magnetic field is along the axes of the dipole tensor permits a determination of the relative orientations of the two nitroxyl nitrogen hyperfine tensors and the orientation of the dipole tensor relative to the hyperfine tensors.[50] They found that for XII the nitrogen of the oxazolidine ring was in an equatorial position of the piperidine ring and that the piperidine ring was in a chair conformation. In this conformation the z axes of the two nitroxyl hyperfine tensors were approximately perpendicular to each other and the z axis of the dipole tensor was approximately perpendicular to the z axes of both nitroxyl hyperfine tensors. The distinctive feature of the allowed transitions for this conformation is that the nitrogen hyperfine splitting is small for molecules that have the magnetic field aligned with the z axis of the dipole tensor, but for molecules that have the magnetic field aligned with the x or y axes of the dipole tensor the nitrogen hyperfine is equal to about half of the value of A_{zz} for a mononitroxyl. This pattern was also observed in the spectra of II and III which indicated that the conformation of II, III, and XII were similar. Since the nitroxyl A tensor is nearly axial, the value of η (Figure 1) is poorly defined, so in the analysis of the hyperfine splitting of the half-field transitions in II and III the value of η was arbitrarily set equal to zero. The best fits to the spectra were obtained with $\epsilon = 85 \pm 5°$, $A_1 = 90 \pm 10°$, and $A_2 = 20 \pm 10°$ which is in excellent agreement with the results obtained by Michon and Rassat from the allowed transitions in XII. It must be noted that Rassat's method of analyzing the hyperfine splitting of the allowed transitions is only possible when the splitting along the axes of the dipole tensor is well resolved. It would be difficult to apply this approach to spectra of dinitroxyls with small values of r or to spectra in which the value of J is similar in magnitude to the dipolar splitting.

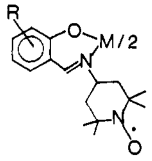


XII

The EPR spectra of the allowed and forbidden transitions for spin-labeled copper complex IV are superpositions of spectra for several species with different values of r and different relative orientations of the tensors for the two unpaired electrons. Complete simulations were not attempted, but simulations of the splittings of the allowed transitions indicated that the two dominant species had values of r of about 5 and 7 Å, respectively. The relative intensity of the half-field transition (5.8×10^{-4}) corresponds to an average value of r of 5.7 Å (eq 8). Since the relative intensity depends on r^{-6}, the average is weighted in favor of molecules with smaller values of r. Thus the value obtained from the half-field transition is in good agreement with the values obtained by computer simulation of the allowed transitions. No structural information is available for IV, but an X-ray structure of copper complex XIII which contains the same coordinated nitroxyl as is present in IV reported copper to nitroxyl oxygen distances of 5.99 to 6.00 Å.[51] Since the unpaired electron is delocalized over the NO bond, the effective distance between the copper and nitroxyl unpaired electrons is less than the copper to oxygen distance. If it is assumed that the midpoint of the NO bond is a better indication of the location of the unpaired electron, the X-ray data indicate an interspin distance of about 5.4 Å. Thus the data obtained from the EPR spectra are quite reasonable.



XIII



M=Cu(II),Zn(II)

XIV

The EPR spectra of the allowed and forbidden transitions for spin-labeled copper complex V also showed contributions from multiple species. Simulation of the spectra of the allowed transitions showed that the two dominant species had values of r of about 6.5 and 8.0 Å, respectively. The overlap of lines for the half-field transitions was too extensive to obtain information on the relative orientations of the dipole tensor and the nuclear hyperfine tensors, but the relative intensity of 1.9×10^{-4} indicated an average value of r of 6.9 Å. Again the average is weighted toward the smaller values of r but agrees well with the results obtained from the allowed transitions. X-ray crystallographic studies have been reported for three metal complexes XIV which contain the same coordinated nitroxyl as is present in V. The metal to nitroxyl oxygen distances in these complexes ranged from 6.53 to 7.04 Å.[52-54] A somewhat smaller value is expected for the interspin distance. Thus the EPR results are in good agreement with the data available for closely related complexes. The variation in the copper to oxygen distance in the three crystal structures indicates the conformational flexibility of these ligands.

X-band EPR spectra of the allowed and forbidden transitions for dinitroxyl VI are shown in Figure 4. The value of D in this case is about the same size as the nitrogen hyperfine splitting so it cannot be determined by inspection of the allowed transitions. The relative intensity of the half-field transition extrapolated to infinite dilution was 5.0×10^{-5} which corresponds to $r = 8.6$ Å (eq 8). Rassat et al. obtained a value of $r = 9.0$ to 9.3 Å for VI based on the temperature dependence of the line widths in fluid solution.[10] In a single-crystal study of VI doped into the analogous diamagnetic diamine, Nakajima found $r = 8.2$ Å.[55] There were

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(50) Michon, J.; Rassat, A. *Tetrahedron* **1980**, *36*, 871–876.

(51) Guseinova, M. K.; Mamedov, S. D. *Zh. Strukt. Khim.* **1978**, *19*, 515–521 (pp 445–450 in translation).

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(53) Guseinova, M. K.; Mamedov, S. D. *Zh. Ztrukt. Khim.* **1978**, *19*, 702–710 (pp 603–609 in translation).

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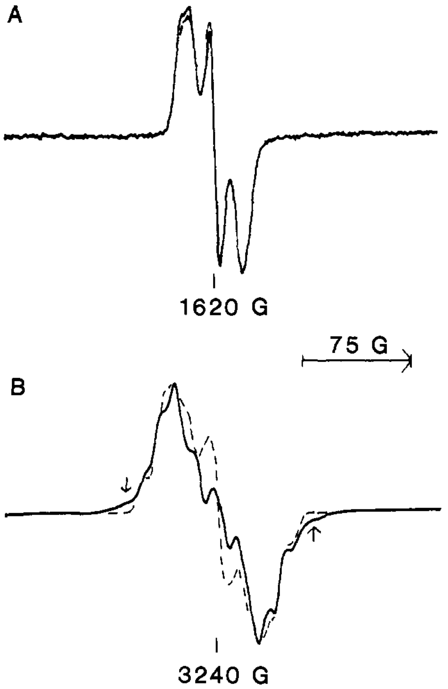

Figure 4. X-band (9.10 GHz) EPR spectra of 5.0×10^{-3} M dinitroxyl VI in a 4:1 toluene/THF glass at −180 °C: (A) 400-G scan of the half-field signal obtained with 5-G modulation amplitude and 200-mW power; (B) 400-G scan of the allowed transitions obtained with 0.4-G modulation amplitude and 0.2-mW power. The dashed lines denote the simulations in regions where the simulated spectra do not overlay the experimental curves.

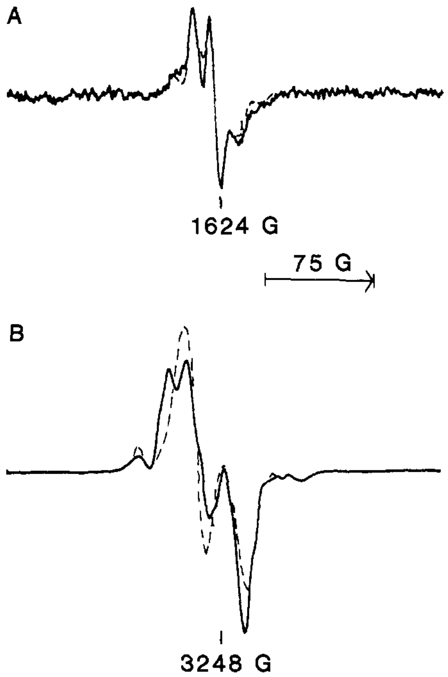

Figure 5. X-band (9.10 GHz) EPR spectra of 4.0×10^{-3} M dinitroxyl VII in a 4:1 toluene/THF glass at −180 °C: (A) 400-G scan of the half-field signal obtained with 2.5-G modulation amplitude and 200-mW power and time-averaged for 10 scans; (B) 400-G scan of the allowed transitions obtained with 0.5-G modulation amplitude and 0.1-mW power. The dashed lines denote the simulations in regions where the simulated spectra do not overlay the experimental curves.

several sites in the crystal so he was not able to analyze the orientation dependence of the nitrogen hyperfine splitting and therefore did not obtain detailed information on the relative orientations of the tensors. The EPR spectrum of the half-field transition for diradical VI is shown in Figure 4A. The approximately three-line pattern with spacings of about 16 G is characteristic of A_1 about 90° and a small value of A_2. The intensity of the central line relative to the other two lines was best fit with ϵ about 45°. Since the nitroxyl A tensor is nearly axial, the value of η is poorly defined so it was arbitrarily set equal to zero in the simulations of the spectra. The fluid solution spectra of VI indicated that the value of J was large relative to the g and A values. Simulation of the allowed transitions with the orientation parameters obtained from the half-field transition and $J = 0.5$ cm^{-1}, $r = 9.0$ Å, gave the spectrum shown in Figure 4B. The general features appear reasonable, but there is some discrepancy primarily in the center of the spectrum. Values of r and the orientation parameters obtained from a CPK molecular model of VI in an extended conformation are in good agreement with the values used in the simulation of the allowed transitions. The relative intensity of the half-field signal gave $r = 8.6$ Å which is smaller than the value that gave the best fit to the spectrum of the allowed transitions. Since the intensity of the half-field transition is dependent on r^{-6}, the average value for several conformations is weighted in favor of the ones with the shorter interspin distances. Thus only a small amount of a conformation with a smaller value of r could cause the observed discrepancy in the values of r obtained from the two portions of the spectrum. The small peaks in the wings of the experimental spectrum (marked with arrows in Figure 4B) that are not present in the simulated spectrum also indicate a small contribution from a conformation with a shorter r. This species may also account for some of the discrepancy between the observed and calculated curves at the center of the multiplet.

EPR spectra of the allowed and forbidden transitions for dinitroxyl VII are shown in Figure 5. The relative intensity of the half-field transition extrapolated to infinite dilution was 9.5×10^{-6} which corresponds to $r = 11.3$ Å. An X-ray crystallographic study of VII found a nitrogen–nitrogen distance of 10.32 Å and an oxygen–oxygen distance of 12.85 Å.[56] If it is assumed that the unpaired electron is approximately at the midpoint of the nitrogen–oxygen bond, then r would be the average of the nitrogen–nitrogen and oxygen–oxygen distances which is 11.58 Å. The value obtained from the relative intensity of the half-field transition is in good agreement with this X-ray value. A value of r of 11.2 ± 0.6 Å has been obtained from the second moment of the allowed transition for VII.[57] There is no indication in ref 57 how the exchange and dipolar contributions were separated. The spectrum of the half-field transition for diradical VII is shown in Figure 5A. The observed five-line pattern with approximately equal spacings of about 12 G is characteristic of A_1 and A_2 about 30° and ϵ about 90°. The values of r and the orientation parameters are in good agreement with values obtained from a CPK molecular model of VII in an extended conformation. In fluid solution spectra of VII the absolute value of J has been observed to range from 24 to 38 G depending on the polarity of the solvent.[18,58] It has been noted previously that simulation of the allowed transitions in the frozen solution spectra of VII is difficult because J is about the same size as the dipolar splittings.[59] However, once the orientation parameters and the value of r have been obtained from the line shape of the half-field signal and the relative intensity of the half-field signal, respectively, the only adjustable parameter in the simulation of the allowed transitions is the value of J. Since there is some uncertainty in all of the parameters, it is reasonable to make adjustments in the values obtained from the analysis of the half-field signal, but the range of values to be explored is relatively small. The simulation shown in Figure 5B was obtained with the orientation parameters taken from the half-field transition

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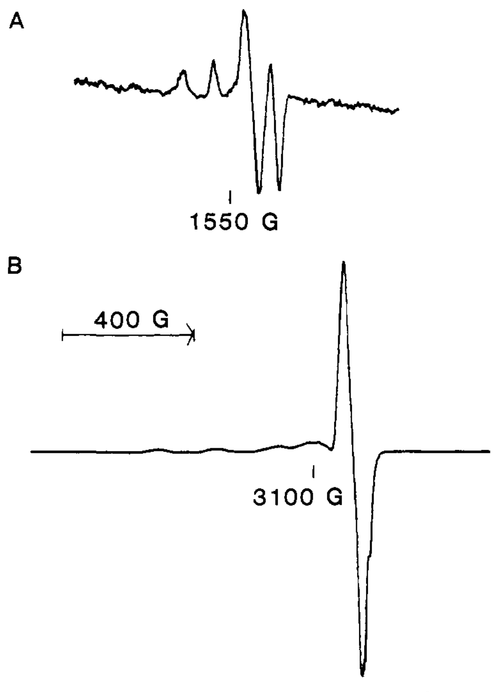

Figure 6. X-band (9.10 GHz) EPR spectra of 5.0×10^{-3} M spin-labeled copper complex X in a 1:1 THF/CH_2Cl_2 glass at −180 °C: (A) 1000-G scan of the half-field transition obtained with 5.0-G modulation amplitude and 200-mW power and time-averaged for 12 scans; (B) 1500-G scan of the allowed transitions obtained with 0.5-G modulation amplitude and 0.4-mW power.

and $r = 11$ Å, $J = -25 \times 10^{-4}$ cm^{-1} (~−25 G). Since the dipolar and exchange splittings are of similar magnitude, the simulated spectrum is sensitive to the sign of J. Satisfactory agreement could not be obtained with a positive value of J. The negative value of J indicated that the singlet was lower in energy than the triplet. Glarum and Marshall found that the value of J for VII in a liquid crystal was +42 G, but their sign convention was the opposite of that used in this paper so they also concluded that the singlet was lower than the triplet.[60] The larger magnitude of J in the liquid crystal than in the toluene/THF glass is consistent with the greater polarity of the liquid crystal than of the toluene/THF glass.

Frequency Dependence of the Relative Intensity. Equation 8 indicates that the relative intensity of the half-field transition is inversely dependent on the square of the spectrometer operating frequency. Spectra of dinitroxyls VI and VII were run at S-band for comparison with the X-band results. Spectra of dinitroxyl II were run at Q-band. The changes in the relative intensity of the half-field transitions confirmed the frequency dependence indicated in eq 8. Although there is some inherent loss of spectrometer sensitivity as the frequency is decreased,[61] the decrease in sensitivity is less than the increase in the relative intensity of the half-field transition. Thus it can be expected that as lower frequency spectrometers become more widely available, they will be very useful in studies of the relative intensity of the half-field transition.

Systems with Three Unpaired Electrons. In some doubly spin-labeled copper complexes, the copper–nitroxyl interaction is much greater than the nitroxyl–nitroxyl interaction. It would therefore seem likely that eq 8 would still be applicable. Spectra were therefore obtained for complexes VIII and IX. Previous analyses of the allowed transitions had assumed that the z axis of the dipole tensor was perpendicular to the z axis of the copper hyperfine tensor.[19] Although molecular models indicated that this was a reasonable approximation, they indicated that the alignment was not exact. Estimates of the values of r for VIII and IX were 7.3 and 7.1 Å, respectively.[19] If the axes were not precisely aligned, the maximum dipolar interaction would not coincide with the turning points in the powder pattern because of the copper hyperfine splitting, and the interspin distance would be overestimated. The values of r obtained from the relative intensity of the half-field transitions were 6.7 and 6.6 Å for VIII and IX, respectively. An X-ray crystal structure of a copper–copper dimer containing the same nitroxyl ligand as in VIII reported copper–oxygen distances of 7.3 to 7.4 Å.[62] If it is assumed that the effective location of the nitroxyl unpaired electron is about midway between the nitroxyl oxygen and the nitrogen, then the X-ray data would give a copper–nitroxyl distance of about 6.7 Å, which is in excellent agreement with the value obtained from the relative intensity of the half-field transition. Further calculations are underway to determine the range of validity for application of eq 8 to three-spin systems.

Application to a Complex of Unknown Geometry. To demonstrate the utility of this method for systems where other approaches could not be used, we have examined the $\Delta M_s = 2$ transition for spin-labeled copper complex X (Figure 6). The large copper hyperfine coupling and the poorly resolved features of the allowed transitions precluded the use of eq 3 to determine the value of r. The relative intensity of the half-field transition was obtained at 2.0×10^{-2}, 1.0×10^{-2}, and 5.0×10^{-3} M. The values were extrapolated to infinite dilution to give relative intensity = 2.2×10^{-5} which corresponds to $r = 9.8$ Å (eq 8). The hyperfine splitting of the half-field signal indicated that the value of ϵ was about 45°. The nitroxyl hyperfine splitting was not resolved in the half-field transition so the values of A_t and A_2 were not defined. CPK molecular models indicated a range of plausible conformations of X with $r = 9.5$ to 11 Å and ϵ about 45°. Thus the results obtained from the half-field signal appear to be fully plausible and may be taken as a current best estimate of the molecular geometry.

Conclusions

The results obtained for molecules of known geometry with values of the interspin distance, r, between 4.5 and 11 Å indicate that the relative intensity of the half-field transition is a reliable indicator of the interspin distance. The hyperfine splitting of the half-field transition can be used to determine the relative orientations of the nuclear hyperfine tensors and the dipole tensor. When the values of r and the orientation parameters have been obtained from the half-field transition, the value and sign of J can be obtained from the allowed transitions for systems in which J is about the same size as the dipolar splitting.

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Registry No. I, 79682-04-5; II, 40932-97-6; III, 33022-15-0; IV, 72442-86-5; V, 72442-72-9; VI, 6146-54-9; VII, 6146-58-3; VIII, 77082-22-5; IX, 77082-21-4; X, 66775-34-6; XI, 2896-70-0.

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