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^{1}H AND ^{13}C ENDOR ON PHENOXYL BIRADICALS RANDOMLY ORIENTED IN FROZEN SOLUTION

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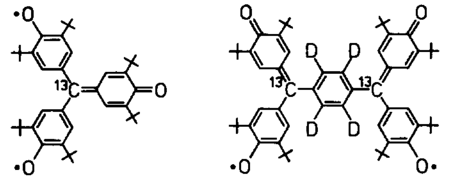
Abstract—ENDOR measurements have been performed on ^{13}C labelled biradicals, namely Yang's biradical and *p*-phenylenebisgalvinoxyl, in frozen solutions. Besides intense ENDOR lines at the free nuclear Zeeman frequencies, hyperfine shifted ^{1}H and ^{13}C ENDOR lines could be detected with excellent signal-to-noise ratios. From these spectra not only the magnitudes, but also the signs of the hyperfine splitting components relative to the zero field splitting parameter D could be derived. It is demonstrated that the sign of D in Yang's biradical must be negative. This may be due to a spin-orbit coupling contribution to the zero field splitting parameter.

INTRODUCTION

ESR investigations of organic radicals with $S \geq 1$ are complicated by the presence of the anisotropic electron spin-electron spin dipolar interaction, which gives rise to the zero field splitting (zfs). Usually, this interaction reduces the resolution of the ESR spectra to the extent that it prevents the measurement of hyperfine coupling constants. A number of studies of organic bi- and triradicals[1-4] have demonstrated that this information can be obtained using ENDOR. So far these studies were concerned with systems in fluid solution or in "soft" glasses, where hyperfine anisotropy is averaged out by molecular motion. Here we report on an ENDOR study of biradicals randomly oriented in solid solution under conditions where molecular motion is frozen out. This study appeared of interest since it could give detailed information on the magnitudes of hyperfine splitting tensor components, as well as their signs relative to the sign of the zfs parameter D.[3,5]

The structure of the two biradicals studied is shown in Fig. 1. They represent examples of two different kinds of triplet species. In Yang's biradical (I) the MO's of the unpaired electrons extend over the whole molecule. Assuming (approximate) trigonal symmetry, the symmetry (z) axis represents the direction of the largest zfs tensor component. The expression for the zfs parameter D is given by $D = (3/4)g^2\beta^2\langle(r_{12}^2 - 3z_{12}^2)/r_{12}^5\rangle$, where r_{12} denotes the distance vector between the unpaired electrons and z_{12} is its projection along the symmetry axis. In Yang's biradical $r_{12} \gg z_{12}$, so that one expects that D should be positive.[3] On the other hand, in II the MO of each unpaired electron, to a first approximation, can be considered to extend over one half of the molecule only.[6] If that view is correct, the direction (z) associated with the largest zfs component is along the axis connecting the centers of gravity of the two electron density distributions. Then, $r_{12} \simeq z_{12}$ so that D must be negative.



I II

Fig. 1. Structural formulas of the biradicals investigated.

ESR spectra of randomly oriented triplets show peaks due to those molecules that have one of their principal zfs axes parallel to the external field.[7] Since the field position in the ESR spectrum is used to select the molecular orientations that will contribute to the ENDOR signal, the basic difference between the two kinds of molecules should be evident in the ENDOR spectra. The structure of Yang's biradical is of special interest, since it shows trigonal symmetry in fluid solution,[1,2,8] whereas studies in solid solution reveal a perturbation of the symmetry.[3,6,9,10] Detailed information on the hyperfine splitting components of I in solid solution could give a better insight in the extent of the perturbation than that offered by ESR and ENDOR-induced ESR.

EXPERIMENTAL

The syntheses of the parent compounds of biradicals I and II, including the ^{13}C labelled systems, have been reported previously.[2,4,11] The biradicals were generated in pure, degassed solvents by oxidation of the parent compounds with PbO_2 or alkaline potassium ferricyanide following standard procedures.[12] Solvents used were toluene, perdeuterotoluene, cumene and 2-MTHF. Solvent changes did not affect the ENDOR spectra noticeably.

ENDOR spectra were recorded with a Varian E-9 X-band ESR spectrometer with a home-built ENDOR accessory[13] and a Bruker ER 220 D ESR spectrometer equipped with a Bruker cavity (ER 200 ENB) and home-built NMR facilities.[14] Typically the ENDOR spectra of I and II were obtained at about 100 K, using 5 mW microwave power, ~200 W rf power corresponding to $B_{NMR} \sim 1$ mT in the rotating frame and a frequency modulation of 10 kHz with a frequency deviation of about ±60 kHz. Field modulation is not used in recording the ENDOR spectra.

RESULTS AND DISCUSSION

For both systems the exchange interaction J is much larger than the hyperfine couplings.[1–4] As a consequence, ENDOR line positions are given to first order by

$$\nu_{\mathrm{ENDOR}} = |\nu_n - M_s A_{ii}^n|, \qquad (1)$$

where ν_n is the free nuclear Zeeman frequency of nucleus n and A_{ii}^n is the component of the hyperfine interaction along the axis i. $M_s = -1, 0$, or $+1$ depending on the electron spin manifold within which the NMR transition is induced. In general, the ESR lineshape given by randomly oriented biradicals is determined by the zfs. To first order, the resonance fields associated with the transitions $|-1, M_I> \leftrightarrow |0, M_I>$ and $|0, M_I> \leftrightarrow |1, M_I>$ are given by:[7]

$$B_{-1\leftrightarrow 0} = \frac{h\nu}{g\beta} + \frac{1}{2}[(3n^2-1)D' + 3(\ell^2 - m^2)E'] \qquad (2)$$

$$B_{0\leftrightarrow 1} = \frac{h\nu}{g\beta} - \frac{1}{2}[(3n^2-1)D' + 3(\ell^2 - m^2)E'] \qquad (3)$$

where ℓ, m, n are the direction cosines of the zfs tensor axes (x,y,z) relative to the field direction. It is clear that field positions can be selected where only one of the electron spin transitions ($-1\leftrightarrow 0$ or $0\leftrightarrow 1$) is pumped in the ENDOR experiment. In that case, one expects to find ENDOR lines at ν_n and either $|\nu_n - A_{ii}^n|$ or $|\nu_n + A_{ii}^n|$. Whether the low or the high frequency line is found depends on the signs of D and A_{ii}^n as well as the field position. A summary of the possible conditions is given in Table 1.

^{13}C *ENDOR of biradicals* I *and* II

Figure 2 shows the ENDOR spectra of ^{13}C labelled Yang's biradical obtained for different field settings. In each spectrum one ^{13}C resonance peak is found apart from an intense peak at the "free" ^{13}C frequency (ν_C). It should be noted that the ν_C line is shifted by 114 kHz to higher frequencies due to a second-order effect.[2] The ^{13}C hyperfine components for the different orientations are collected in Table 2. The absolute values of these components agree quite well with those extracted from the ESR spectrum of I in toluene at 150 K ($|A_{XX}^C| = |A_{YY}^C| = 18.2$ MHz, $|A_{ZZ}^C| = 36.2$ MHz).[2]

Table 1. ENDOR line positions as function of the relative signs of the zero-field (D) and hyperfine splitting (A_{ii}^n) parameters and of the field position

RELATIVE SIGN	FIELD POSITION	ENDOR
Sign (D) = sign (A_{ii}^n)	low z	low frequency
	high xy	
	high z	high frequency
	low xy	
Sign (D) ≠ sign (A_{ii}^n)	low z	high frequency
	high xy	
	high z	low frequency
	low xy	

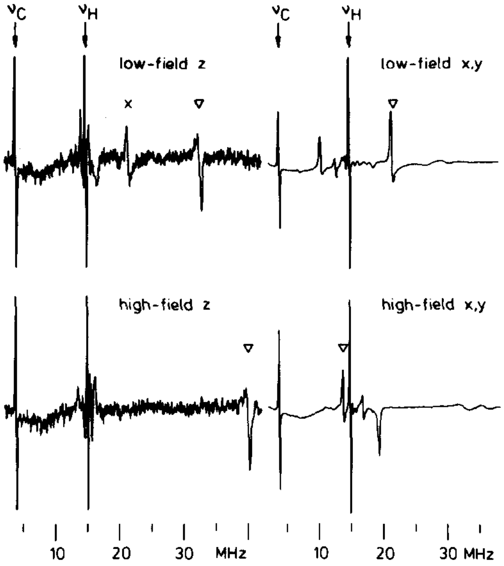


Fig. 2. ENDOR spectra of ^{13}C labelled Yang's biradical (I) in glassy perdeuterotoluene (100 K) for different field settings. The marks (∇) denote the ^{13}C resonance positions. The ENDOR spectrum obtained with the field set on the low-field z peak shows small contributions from the low-field xy component (x).

For the case that I has trigonal symmetry, the ^{13}C hyperfine tensor will have axial symmetry as well, with the axial component given by A_{zz}^C and the perpendicular component by $A_{xx}^C = A_{yy}^C$. It is evident from the ENDOR spectra and Table 1 that the two ^{13}C hyperfine components have the same sign as D. It follows that, for axial symmetry, the isotropic ^{13}C coupling constant is given by $|a^C| = \frac{1}{3}|A_{zz}^C + 2A_{xx}^C| = 23.6$ MHz which is close to the value of 24.2 MHz found in fluid solution.[2] One may conclude that the perturbation of the trigonal symmetry (evident in the solid solution ESR,[6,9,10] ENDOR-induced ESR[3] and possibly the ^{1}H ENDOR spectra) does not affect the ^{13}C hyperfine splitting noticeably. The fact that the widths and shapes of the ^{13}C ENDOR lines obtained with xy field settings are comparable to those with z field settings (single-crystal-like) provides direct experimental evidence that the ^{13}C hyperfine tensor has axial symmetry.

^{13}C ENDOR lines could also be detected for biradical II in solid solution with the field set on the turning points (z peaks) in the ESR spectrum. With the low field z setting we find: $\nu_C = 3.65$ MHz and $|A_{zz}^C| - \nu_C = 5.98$ MHz, with the high field z setting: $\nu_C = 3.71$ MHz and $|A_{zz}^C| + \nu_C = 13.40$ MHz. These data yield a value of $|A_{zz}^C| = 9.7$ MHz. It should be noted that the ^{13}C hyperfine components in II could not be extracted reliably from the rigid-matrix ESR spectrum. From the ^{13}C ENDOR line positions it follows that A_{zz}^C and the zfs parameter D must have the same sign. As pointed out before, the direction associated with the largest zfs component in II, i.e. the z axis, corresponds to the axis joining the two ^{13}C nuclei (*cf* Fig. 1). Therefore, A_{zz}^C represents one of the *in-plane* ^{13}C hyperfine components in this case.

Due to the lack of axial symmetry of II and since the ^{13}C hyperfine components are comparable in magnitude to the zfs parameters (D = 55 MHz, E = 3 MHz[3]), there are no field settings in the center of the ESR spectrum that can be identified with a well-defined range of orientations of the molecule. Consequently, the out-of-plane component of the ^{13}C hyperfine tensor cannot be determined directly. However, it is reasonable to assume that the tensor is close to axially symmetric and that the principal components have the same sign. In that case, the out-of-plane component can be determined by using the information on the in-plane component and the isotropic ^{13}C coupling constant derived from fluid solution spectra ($|a^{C}| = 13.70$ MHz[4]). These data give an absolute value for the out-of-plane ^{13}C hyperfine component of 21.7 MHz. It is of interest to note that the values of the ^{13}C hyperfine components in II are roughly one half of the corresponding values in I. This is consistent with the fact that in II each electron can be considered to spend half its time on each side of the biradical (the exchange interaction is large compared to the hyperfine interaction). As a consequence, the spin density at a given position is reduced by a factor of two. The value of A^{C}_{zz} confirms the conclusion that in II the axis for which the largest dipole–dipole splitting is found in the ESR spectrum must lie in the molecular plane.

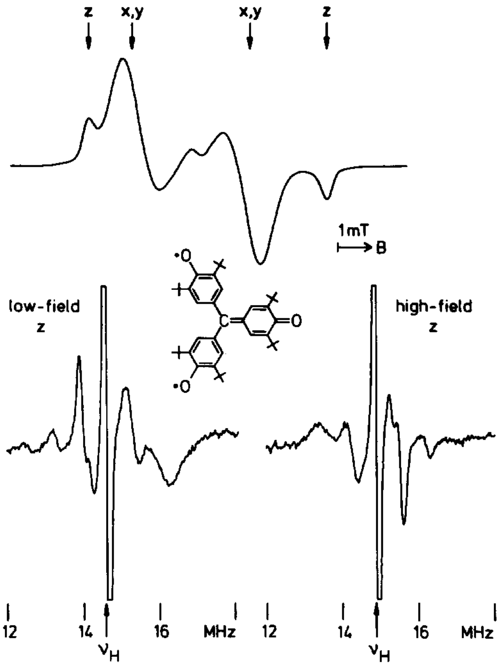


Fig. 3. Rigid-matrix ESR (top) and ^{1}H ENDOR (bottom) spectra of Yang's biradical (I; unlabelled) in glassy perdeuterotoluene at 100 K. The ENDOR spectra were taken with the field set on the low- and high-field z peaks of the ESR spectrum, respectively.

^{1}H *ENDOR of Yang's biradical*

Figure 3 shows the ESR spectrum of Yang's biradical (I; unlabelled) in glassy toluene, as well as the ^{1}H ENDOR spectra obtained with the field set on the low and high field turning points. Figure 4 shows the effect of a temperature change on the ENDOR spectra obtained with high z and high xy field settings. The z as well as the xy spectra exhibit an intense line at the free proton frequency (ν_H) and a set of hyperfine shifted peaks. As expected, the positions of the latter relative to ν_H are reversed when switching from the high z and xy settings to the corresponding low field positions. The hyperfine splittings derived from the spectra are summarized in Table 2.

An earlier analysis[15] of the hyperfine coupling components in Coppinger's radical establishes that the two prominent high frequency peaks in the xy spectrum given in Fig. 4 must be assigned to the aromatic protons. According to the analysis the hyperfine coupling is positive along any direction in the xy plane. Therefore, the high frequency ENDOR line positions associated with the high field xy setting implies that $D < 0$ (*cf.* Table 1). In addition to the resonance peaks due to aromatic protons, the xy spectra exhibit resonances closer to the strong ν_H peak assigned to the methyl protons. As shown in Fig. 4, the intensities of these resonances show a pronounced temperature dependence not found for the peaks attributed to the aromatic protons. The temperature dependence probably must be attributed to a "freezing-out" of the rotation of the sterically hindered t-Bu groups.

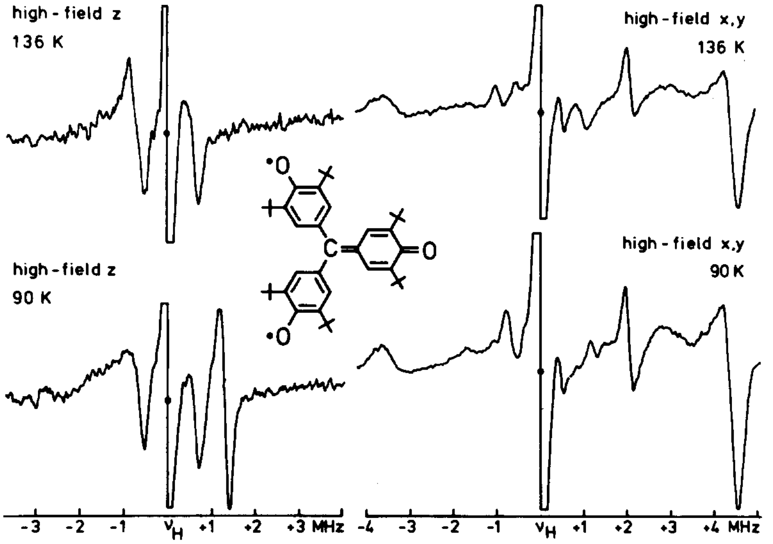


Fig. 4. ^{1}H ENDOR spectra of Yang's biradical (I; unlabelled) for the high z and xy field settings at 90 K and 136 K.

Table 2. ^{1}H and ^{13}C hyperfine coupling components (MHz) (estimated errors ±0.05 MHz except where noted otherwise)

	I† A_{xx}, A_{yy}	I† A_{zz}	II‡ A_{zz}
^{1}H	+4.40*	+1.3 $\pm$ .2	+2.8 $\pm$ .2*
	+2.04*	+0.66	+1.95*
	+0.92	−0.42	+0.52
	+0.46	−0.63	
		−1.33	
^{13}C	−17.45	−36.0	−9.66

† Toluene, 100 K.

‡ Cumene, 100 K.

* Aromatic proton

Figure 4 shows that the temperature dependence is even more pronounced in the spectra obtained with the z field settings. Of the five hyperfine-shifted peaks evident in Fig. 3 and listed in Table 2 at least two are strongly reduced in intensity with increasing temperature. Two others are unaffected by temperature changes. Assigning the temperature dependent resonances to t-Bu protons, two prominent hyperfine shifted peaks remain to be accounted for.

If Yang's biradical has trigonal symmetry the z settings correspond to an orientation of the symmetry axis parallel to the external field. For symmetry reasons, one expects to observe two resonance lines (not counting the ν_H peak). One for the ring protons and one for the t-Bu protons, provided that the t-Bu groups are rotating rapidly. Indeed it appears that with increasing temperature only two hyperfine shifted lines remain in the z spectra. Nevertheless, the assignment of one to a set of equivalent aromatic protons and the other to a set of equivalent t-Bu protons is unsatisfactory since the relative intensities of the two peaks is unaffected by temperature changes. As pointed out in the Introduction, there is experimental evidence that the trigonal symmetry of I is perturbed in solid solution.[3,6,9,10] Hence it is feasible that both temperature independent lines are due to aromatic protons. At this time no definitive assignment of the proton lines in the z spectra can be given, also the temperature dependence of the proton ENDOR spectra is not yet fully understood. We hope to be able to resolve these questions in the near future through studies of ^{2}H labelled Yang's biradical.

In II the z field settings give information on the proton hyperfine coupling components along the axis connecting the two ^{13}C nuclei (*cf* Fig. 1). With a high z field setting aromatic proton peaks are found at $\nu_H - 2.8$ and $\nu_H - 1.95$ MHz. Since the sign of the aromatic proton hyperfine couplings along this axis is predicted[15] to be positive, we conclude that $D < 0$ (*cf* Table 1). The only additional hyperfine shifted peak is found at $\nu_H - 0.52$ MHz. Its intensity varies with temperature so that we attribute it to the t-Bu protons. Additional t-Bu proton resonances may be buried under the strong ν_H peak.

The sign of D

From the positions of the ^{13}C ENDOR lines obtained for a given field setting it could be deduced that in both biradicals the zfs parameter D and the ^{13}C hyperfine components have the same sign. ESR and TRIPLE measurements have shown that the isotropic ^{13}C coupling constants in I and in galvinoxyl radicals (like II) are negative.[2,16] Hence, we conclude that $D < 0$ in both systems. This conclusion is supported by the proton ENDOR data (*vide supra*). As pointed out earlier, assuming that the zfs in these systems stems completely from the dipole–dipole interaction between the electron spins, D is expected to be negative in II in agreement with the experimental result. On the other hand, we expected to find $D > 0$ in I. The non-planarity due to steric hindrance[17] or small deviations from trigonal symmetry are unlikely to reverse the sign of D. A possible explanation for the negative sign of D in Yang's biradical could be the presence of negative spin densitites in this odd-alternant system.[18] While the effect of the negative spin densities cannot be assessed in the absence of detailed theoretical calculation, it will be shown in the following that spin-orbit coupling provides a contribution of the right magnitude and sign to give rise to a sign reversal of D. It is evident from the ESR spectrum shown in Fig. 3 that the g value is markedly anisotropic, i.e. there is a significant spin-orbit contribution to the g factor. This suggests the possibility that the unexpected sign of D may be due to a spin-orbit coupling contribution to the zfs parameters. Such effects have been studied experimentally and theoretically for the lowest triplet states of aromatic ketones[19] and carbonyl compounds.[20] In some of these cases spin-orbit interaction turned out to be extremely important, affecting not only the magnitudes but also the signs of the parameters. Previously a simple proportionality between the spin-orbit contribution to D and the g shift $\Delta g_{zz} = g_{zz} - g_e$ has been derived by assuming a mixing of the lowest $n\pi^*$ and $\pi\pi^*$ triplet states. Such a proportionality between the components of the spin-orbit part $\mathbf{D}^{so}$ of the zfs tensor and the g-shift tensor $\mathbf{\Delta g}$ has been shown to be quite general for the Russell–Saunders coupling case (e.g. for transition metal ions).[21] The relation is given by

$$\mathbf{D}^{so} = \frac{1}{2}\lambda\mathbf{\Delta g}, \tag{4}$$

where λ is the spin-orbit coupling parameter of the (identical) atom(s) mainly contributing to $\mathbf{\Delta g}$.

Application of eqn (4) to Yang's biradical yields (for axial symmetry)

$$D^{so} = \frac{1}{2}\lambda_O(g_{zz} - g_{xx}), \tag{5}$$

assuming that the spins are confined to the O atoms. Inserting the observed values $g_{zz} = 2.0031$ and $g_{xx} = g_{yy} = 2.0056$[3] and using $\lambda_O = 152\,\text{cm}^{-1}$,[22] the relation does, in fact, yield a ***negative*** value of D^{so}. However, the magnitude of D^{so} ($\simeq -6000$ MHz) exceeds the experimental value of $|D|$ (95 MHz) by several orders of magnitude. This discrepancy cannot be explained by spin delocalization or structural deformation, but must be attributed to the fact that eqn (4) is not applicable to ***molecules***, where the Russell–Saunders coupling scheme usually breaks down. Exceptions would only occur in those special situations, where the energy gaps between states of different spin multiplicity are so large that any mixing can be neglected.[20] The breakdown of Russell–

Saunders coupling becomes particularly obvious for biradicals of the type studied here, where the one-center spin-orbit interactions at the O atoms are clearly larger than any two-center spin-orbit couplings.

In order to obtain at least a semiquantitative estimate of the correct magnitude of D^{so}, we have applied the quite general theory of Glarum.[23] In this theory the different contributions to Δg and D^{so} from various one-electron promotions within a particular multiplet state or between states of different multiplicity are derived. The theory shows that, apart from triplet–triplet excitations which contribute to *both* Δg and D^{so} and produce a simple relation of the form of eqn (4), there also can be contributions to D^{so} *alone* from triplet–singlet excitations. Triplet–triplet ($\Delta E^{(3)}$) and triplet–singlet ($\Delta E^{(1)}$) energy gaps (involving electron promotions between identical orbitals) are of similar magnitudes in biradicals, differing only in the comparatively small exchange energy J, i.e. $J \ll \Delta E^{(1)} \simeq \Delta E^{(3)}$ and $\Delta E^{(1)} = \Delta E^{(3)} + J$ with $J > 0$ for ground state triplets. Hence, important contributions to D from such triplet–singlet excitations are to be expected. An essential point is that these contributions are *opposite* in sign to the contributions from triplet–triplet excitations. If only the two lowest *excited* singlet and triplet states, produced by promotion of a non-bonding (lone-pair) electron on an oxygen atom to the lowest half-filled π-orbital, are considered ($\pi - \pi^*$ excitations give negligible contributions to D^{so} and Δg) it can be shown, using the results of Glarum,[23] that

$$D^{so} = A\left(\frac{1}{\Delta E^{(3)}} - \frac{1}{\Delta E^{(1)}}\right), \qquad (6)$$

where $A/\Delta E^{(3)} = \lambda_0 \Delta g/4$. This result can be approximated by

$$D^{so} \simeq \frac{1}{4}\lambda_0 \Delta g \frac{J}{\Delta E^{(3)}}. \qquad (7)$$

The appearance of J is physically reasonable since in the limit of complete separation of the electron spins ($J = 0$) D^{so} must vanish.

In comparing eqn (7) with eqn (4), we note that the sign of D^{so} is retained whereas the magnitude is now reduced by the (positive) energy ratio $J/\Delta E^{(3)}$. According to Brown,[21] $\Delta E^{(3)} \simeq \Delta E(n \rightarrow \pi) \simeq 24{,}000\,\mathrm{cm}^{-1}$. The value of J is expected to be in the order of several kcal/mol, i.e. $J \simeq 300 - 1000\,\mathrm{cm}^{-1}$ for the ground state triplet molecule I.[12,24] This yields $D^{so} \simeq -40$ to -120 MHz which is of the same order of magnitude as the observed value of D. In conclusion, therefore, our assumption that spin-orbit coupling can account for the observed sign of D in I appears to be justified. For biradical II, where $J \simeq -3\,\mathrm{cm}^{-1}$,[12] the spin-orbit contribution to D can be neglected.

It is of interest to consider the results reported by Mukai[17] in the light of this interpretation. Mukai studied the solid solution ESR spectra of Yang's biradical (I; unlabelled) and I in which the two t-Bu groups on one phenyl ring were replaced by Me groups (2 Me–I). He found $|D| = 65.2$ MHz in 2 Me–I vs $|D| = 95.5$ MHz in I. Moreover, the g-tensor anisotropy in 2 Me–I is much less than in I, with $g_{xx} = 2.0046$, $g_{yy} = 2.0041$ and $g_{zz} = 2.0035$. In the interpretation of these results Mukai assumes that the D values are purely dipolar in origin. From the (apparent) reduction in D upon going from I to 2 Me–I he concludes that the twist angles of the phenyl rings in the latter compound are larger than in I. Clearly, a more satisfactory explanation can be offered using our knowledge of the sign of D in I. Actually D increases upon going from I to 2 Me–I. This increase is consistent with the expected decrease in twist angles in 2 Me–I, which will *increase the dipolar contribution to D*. More importantly perhaps, it is also consistent with the *decreased spin-orbit contribution to D*, which is mirrored in the smaller g-value anisotropy.

CONCLUSIONS

It has been shown that ENDOR spectra of organic triplet state molecules randomly oriented in a rigid matrix are obtained readily. In the applications discussed here, spectra with excellent signal-to-noise ratio were obtained well above liquid nitrogen temperature. Biradicals formed upon dimerization of ketyl anion radicals[25] also have been found to give strong ENDOR signals under similar conditions.[26]

The ENDOR spectra can be of aid in determining the electronic and geometric structure of the triplet state molecules. Specifically, the spectra obtained with different field settings can give an insight in the orientation of the principal axes of the zfs tensor, they can give information on the sign of the zfs parameter D and they contain detailed information on the hyperfine splitting tensors of the magnetic nuclei present. So far no definitive analysis of the proton ENDOR spectra can be given. For non-planar triplets like the ones considered here, it may prove impossible to extract information on the principal components of the proton hyperfine tensors directly from the spectra. However, the spectra could be of value in checking the results of theoretical calculations. Namely, given the results of a calculation of the spin density distribution, one can calculate the ENDOR spectrum expected for a given (range of) orientation(s) of the molecule with respect to the field direction.

Finally, it is noted that ENDOR studies could contribute to the understanding of the structure of triplet state systems formed by dimerization of transition metal complexes[27] and by association of a transition metal complex with a spin label.[28]

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