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Some Environmental Effects on the shf Lines in the ESR Spectra of Vanadyl Tetraphenylporphin

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The ESR spectra of vanadyl tetraphenylporphin (VOTPP) have been studied in a number of organic matrices, with special attention paid to the resolution of the nitrogen shf lines. The matrices were classified into three groups according to their effects on the resolutions of the vanadium hf lines and of the nitrogen shf lines. In the A-group matrices, the spectra of VOTPP displayed well-resolved hf lines, accompanied by shf splittings; in the B-group matrices, the spectra gave rise to well-resolved hf lines, but without shf splittings, and in the C-group matrices, the hf lines were resolved only poorly. It is suggested that a high dispersion of VOTPP molecules is required for the higher resolution of spectra.

The ESR spectra of vanadyl porphyrin complexes have been studied by many workers,[1–4] but superhyperfine (shf) splittings due to the ligand nitrogen nuclei($I=1$) have been only poorly characterized.

For example, it was shown by O'Reilly[1] and Roberts *et al.*[2] that each of the vanadyl complexes of etioporphyrin, I and II, the mesoporphyrin IX dimethylester, and the deuteroporphyrin IX dimethylester gave the hyperfine (hf) structure due to the vanadium nucleus ($I=7/2$), but none had any observable shf splittings. Kivelson *et al.*,[3] however, found that nitrogen shf lines could be resolved when vanadyl tetraphenylporphin (VOTPP) was diluted in the frozen matrices of $CHCl_3$ and CS_2 although the spectra of VOTPP in other matrices failed to yield any evidence of shf splittings. On the contrary, Assour[4] shortly afterward reported that VOTPP did not display the shf splittings even in the $CHCl_3$ and CS_2 matrices.

More recently, the present authors,[5] studying the spectra of vanadyl phthalocyanine (VOPc) diluted in the matrices of conc. H_2SO_4, α-chloronaphthalene, quinoline, metal-free phthalocyanine, and zinc phthalocyanine,[6] found that the spectra of VOPc can give rise to nitrogen shf splittings in all the matrices investigated. This result was in contrast with those of previous studies of vanadyl porphyrin complex, and stimulated us to reinvestigate the spectra of VOTPP diluted in many kinds of organic matrices, with special attention being paid to the effects of matrix states on the resolution of the shf lines. As a result, we found, contrary to the previous authors,[3,4] that shf lines could be easily detected in almost all the matrices and that their resolution is associated with the homogeneity of the matrix environment of VOTPP. The present paper will report the results of such investigations.

Experimental

Materials. *Vanadyl Tetraphenylporphin (VOTPP)*: Tetraphenylporphin (H_2TPP) and its vanadyl complex (VOTPP) were prepared according to the procedure in the literature[7] and were purified by recrystallization from benzene. The thin-layer chromatograph[8] showed few impurities to be present.

Organic Matrices: The various organic solvents and crystals used as diluents for VOTPP are listed in Table 1. These were all commercial samples either of a reagent grade or of an extra pure grade; all of them except α- and β-methylnapthalene, *o*-dichlorobenzene, triphenylphosphate, and triphenylmethane were further purified, either by distillation or by recrystallization.

Preparation of Diluted VOTPP Samples. *VOTPP in Frozen Organic Solvents*: The VOTPP was dissolved in various organic solvents in a concentration of $1-5\times10^{-3}$ mol/l at room temperature. Each solution was then subjected to rapid cooling with liquid nitrogen to form either a polycrystalline or glassy matrix. In the present paper, the expression "polycrystalline state" will arbitrarily be used to signify the matrix state accompanied by polycrystals which scatter light strongly, while the term "glassy state" indicates the transparent matrix state. The two states were easily distinguishable from one another with the naked eye. The matrix states for the respective frozen solutions are shown in Table 1 in terms of "p" (polycrystalline state) and "g" (glassy state) respectively.

VOTPP in Organic Crystals: The VOTPP samples diluted in organic crystals were prepared in the following way otherwise stated. After the VOTPP had been dissolved in 100—500 times their weight of melts of organic crystals which had been kept at a temperature 50—60 °C above their melting points, the melts were suddenly cooled to 77 K with liquid nitrogen. Although most of the samples formed excellent glasses at this stage, they were later warmed to room temperature. This procedure generally gave finely polycrystalline matrices.

VOTPP in H_2TPP: A chloroform solution containing VOTPP and H_2TPP in a weight ratio of 1 : 200 was poured into a large amount of methanol, causing finely-dispersed precipitates to separate out. The precipitates thus obtained were washed with methanol and dried. The powder was then heat-treated in a vacuum at 300 °C.

Measurements of the ESR Spectra. The ESR spectra were recorded with a JEOL spectrometer, Model JES P-10 (X-band), using 100 KHz field modulation. The magnetic field was calibrated with an ESR marker, MgO: Mn^{2+} powder, supplied by JEOL. The *g*-values were determined using powdered DPPH, with $g=2.0036$ as the standard.

The VOTPP samples diluted in frozen organic solvents were measured at 77 K, while those in organic crystals were measured mainly at room temperature. Degassing was not carried out for all the samples, since the effect of oxygen on the linewidths was preliminarily found to be negligible for VOTPP in the $CHCl_3$, toluene, H_2TPP, and triphenylphosphine matrices.

Results and Discussion

As is summarized in Table 1, the organic solvents and crystals employed as the diluents of VOTPP were

TABLE 1. RESOLUTION OF hf AND shf LINES IN ESR SPECTRA OF VOTPP DILUTED IN VARIOUS ORGANIC MATRICES

	Matrices		Vanadium hf lines	Nitrogen shf lines	Diluted states of VOTPP
	Frozen organic solvent[a]	Organic crystals			
A-Group	Toluene(g) *o*-Xylene(p) *m*-Xylene(p) Xylene(g)[b] α-Methylnaphthalene(g) $CHCl_3$(p) CH_2Cl_2(p) Quinoline(g) α-Chloronaphthalene(p) *o*-Dichlorobenzene(p) *o*-Fluorotoluene(p)	H_2TPP Triphenylmethane *sym*-Triphenylbenzene Triphenylphosphine Triphenylphosphate[d]	well resolved	resolved	well dispersed (homogeneous environment)
B-Group	*p*-Xylene(p) CS_2(p)[c] Tetrahydrofuran(p) α-Methyltetra-hydrofuran(g) Pyridine(p) Isoquinoline(p)		well resolved	unresolved	well dispersed (inhomogeneous environment)
C-Group	Benzene(p) CCl_4(p)	Naphthalene β-Methyl-naphthalene	poorly resolved	unresolved	aggregated

a) (g): "glassy state", (p): "polycrystalline state". b) A commercial mixture of three isomeric xylenes. c) Many attempts to obtain an evidence of shf splittings in the CS_2 matrix were unsuccessful. This agreed with the result by Assour[4] rather than that by Kivelson *et al.*[3] d) See text.

classified conventionally into three groups according to their effects on the resolutions of the vanadium hf lines and the nitrogen shf lines. In the "A group" matrices, the spectra of VOTPP gave rise to well-resolved vanadium hf lines, accompanied by nitrogen shf splittings; in the "B-group" matrices, the spectra gave rise to well-resolved hf lines, but without any evidence of shf splittings, and finally, in the "C-group" matrices, only poorly-resolved hf lines were observed.

Vanadium hf Lines. As has been reported in the literature,[3,4] the spectra of VOTPP showed, in general, eight hf lines due to the vanadium nuclei (I= 7/2) in the matrices employed. The present work also showed such a characteristic. However, the apparent linewidth of hf lines was found to depend upon the kind of matrix species, hence causing the degree of hf resolution to differ from one matrix to the other. The linewidths observed in the A-group and B-group matrices were much smaller than those observed in the C-group matrices. Some representative spectra are illustrated in Figs. 1 and 2.

The interpretation of these spectra follows closely the method developed by Sands[9] and Bleaney.[10] The spin Hamiltonian used in the one reflecting the axial symmetry:

$$\begin{aligned}\mathscr{H} &= \beta[g_{//}H_zS_z + g_{\perp}(H_xS_x+H_yS_y)] \\ &\quad + A_{//}I_zS_z + A_{\perp}(I_xS_x+I_yS_y) \qquad (1) \\ S &= 1/2, \quad I = 7/2\end{aligned}$$

where $A_{//}$ and $A_{\perp}$ are the vanadium hf coupling constants and where the other symbols have their usual meanings. The spectrum shown in Fig. 1 is composed of two distinct set of hf lines that correspond to $g_{//}$ and $g_{\perp}$; the two weak peaks at the low-field peaks and the three high-field peaks correspond to $g_{//}$, while the strong central peaks are associated with $g_{\perp}$. However, such a spectral feature is rather obscure in the spectrum shown in Fig. 2 because of its larger linewidth. The spin Hamiltonian parameters obtained from some of the A-group and B-group matrices are summarized in Table 2.

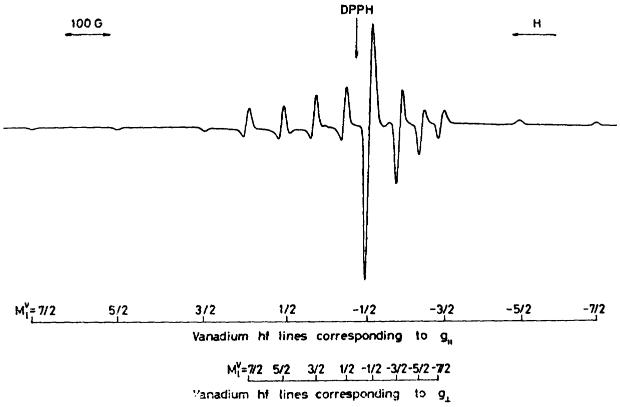

Fig. 1. ESR spectrum typical for VOTPP diluted in the A-group and B-group matrices.
Matrix: Toluene, Concentration of VOTPP: [VOTPP]=2.9×10^{-3} M, Temperature: T=77 K.
(Two sets of vanadium hf lines that correspond to $g_{\parallel}$ and $g_{\perp}$ are indicated at the bottom of the figure. M_I^V refers to the nuclear-spin quantum number of the vanadium atom and is assigned on the basis of the negative values of hf constants.)

Since a smaller linewidth is usually taken to imply smaller magnetic interaction between the neighboring VOTPP molecules, it may be suggested that VOTPP

Table 2. Electron spin resonance data of VOTPP diluted in organic matrices

Matrices	$g_{//}$	$g_{\perp}$	$A_{//}$ ($\times 10^{-4}$cm^{-1})	$A_{\perp}$ ($\times 10^{-4}$cm^{-1})	Average separation of shf multiplets (G)
Toluene	1.960	1.985	160	56	~2.8
$CHCl_3$	1.962	1.986	159	55	2.7~2.9
CH_2Cl_2	1.984	1.984	156	54	2.7~3.0
α-Methyltetrahydrofuran	1.963	1.984	157	55	unresolved
Pyridine	1.964	1.984	157	54	unresolved
H_2TPP	1.961	1.986	160	57	2.6~2.8
Triphenylphosphine	1.960	1.985	159	57	~2.8

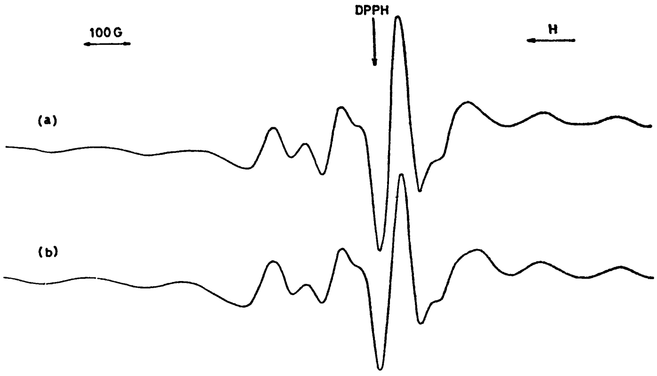

Fig. 2. ESR spectrum typical for VOTPP diluted in the C-group matrices and that obtained from the polycrystalline VOTPP samples.
(a) Matrix: Benzene, [VOTPP]$=1.5\times 10^{-3}$ M, $T=77$ K. (b) Polycrystalline VOTPP, $T=77$ K.

molecules are highly dispersed in the A-group and B-group matrices, without any intermolecular interactions such as association and aggregation. It is interesting to note that the apparent hf linewidth observed in the A-group matrices did not differ much from that observed in the B-group matrices, irrespective of their different effects on the shf resolutions. This aspect will be discussed below.

On the other hand, the spectra observed in the C-group matrices displayed an extraordinarily large linewidth, indicating that strong magnetic interactions between neighboring VOTPP molecules exist in these matrices. Moreover, the spectral line shape was quite similar to that observed for the polycrystalline VOTPP sample, as is shown in Fig. 2. It can, therefore, be presumed that VOTPP molecules are present in either a crystalline or an aggregated form in the C-group matrices. Probably, the aggregation of the VOTPP molecules proceeded during the course of cooling with liquid nitrogen. Actually, microcrystals of VOTPP were observed in the frozen matrix of benzene. Moreover, some finely-dispersed precipitates of VOTPP were perceptible when the frozen CCl_4, naphthalene, and β-methylnaphthalene solutions were thawed.

Nitrogen shf Lines. When ESR spectra were recorded with a small amplitude of the field modulation such as 0.5 G, some of the vanadium hf lines were further split into shf lines due to the magnetic interaction between the V^{4+} electron and the pyrrole nitrogens. Typical examples are illustrated in Figs. 3 and 4. The matrices which gave rise to shf splittings are listed in Table 1, where it is apparent that the great majority belong to the A-group. This result might be compared with the previous results[3,4] which showed that the spectra of VOTPP seldom gave rise to shf splittings.

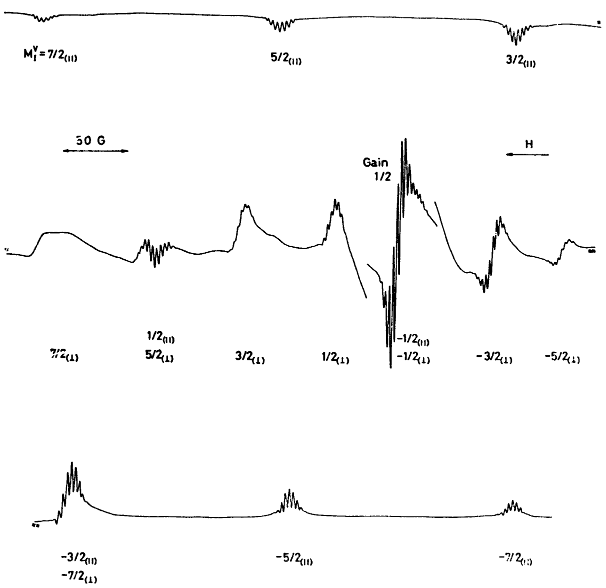

Fig. 3. Nitrogen shf splittings recorded for VOTPP diluted in the $CHCl_3$ matrix. [VOTPP]$=2.9\times 10^{-3}$ M, $T=77$ K.

Judging from the spectral features of the vanadium hf lines in various matrices, it seems very likely that a high dispersion of VOTPP molecules through the matrices is essential for the resolution of shf lines, although the state of dispersion alone would not be sufficient to meet the requirements.

In the A-group matrices, the best resolution of shf lines was recorded from the $CHCl_3$ matrix. It can be seen from Fig. 3 that each of the hf lines is further split into shf multiplets, which are apparently composed of nine equally-spaced lines of varying intensities. Their average separations were 2.9 and 2.7 gauss for the parallel and perpendicular hf components respectively, indicating that the nitrogen shf interaction is nearly isotropic.

The shf Hamiltonian ($\mathscr{H}_{\text{shf}}$) describing the system of this sort can generally be expressed as.[11]

$$\mathscr{H}_{\text{shf}} = \boldsymbol{S}\cdot\sum_{\text{n}} \boldsymbol{A}_{\text{n}}\cdot\boldsymbol{I}_{\text{n}} \tag{2}$$

where $\boldsymbol{A}_{\text{n}}$ and $\boldsymbol{I}_{\text{n}}$ refer to the shf tensor and the nuclear spin operator for the ligating nitrogen atom, n, respectively. Since the shf tensors, $\boldsymbol{A}_n$, have different functional forms for different nitrogen atoms in terms of the molecular coordinates (x,y,z), it is a rather complicated problem to derive the resonance field from Eq. (2). However, if one assumes that the shf tensors are isotropic and that the four nitrogen ligands are magnetically equivalent, Eq. (2) can simply be rewritten as:

$$\mathscr{H}_{\mathrm{shf}} = a^{\mathrm{N}}(S_zI_z^{\mathrm{N}}+S_xI_x^{\mathrm{N}}+S_yI_y^{\mathrm{N}}) \qquad (3)$$

where a^{N} represents the isotropic shf constant and where I_z^{N}, I_x^{N}, and I_y^{N} are the sums of the nitrogen nuclear-spin components in the z, x, and y directions respectively.

One can, then readily obtain the predicted spectrum in which each of the vanadium hf lines is split into 9 shf components, with an equal separation of a^{N} and with the intensity ratio of 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1. The shf multiplets observed on the hf components other than that corresponding to $M_{\mathrm{I}}^{\mathrm{V}}=-1/2$ are, in fact, consistent with this expectation, with the isotropic shf constant being approximated as $a^{\mathrm{N}}=2.8$ G. The observation of at least 13 shf components on the $M_{\mathrm{I}}^{\mathrm{V}}=-1/2$ hf line is not in conflict with the above prediction either, since the $M_{\mathrm{I}}^{\mathrm{V}}=-1/2$ hf line exhibits a "polycrystalline anomalous line" which has previously been discussed.[12)]

It was noted that the resolution of the shf multiplets is rather poor except for the $CHCl_3$ matrix in the A-group matrices. In these matrices, the $M_{\mathrm{I}}^{\mathrm{V}}$ values of the hf components with resolved shf multiplets were also found to differ from those observed in the $CHCl_3$ matrix. As can be seen from Fig. 4, the shf multiplets have a tendency to be resolved not on the parallel hf components but the perpendicular hf components.

Although the accurate determination of the shf constant was difficult due to its poor resolution, the average separation of the shf lines was estimated to range from 2.6 to 3.0 G in the matrices of toluene, xylene, H_2TPP, CH_2Cl_2, and triphenylphosphine. If Eq. (3) is valid in these cases, the above values of 2.6—3.0 G can be regarded as a^{N}, in agreement with the the shf constant, $a^{\mathrm{N}}=2.8$ G, obtained for the $CHCl_3$ matrix.

It follows from the above arguments that the matrices have little effect on the magnitude of the shf constant, while they play a significant role in the resolution of shf multiplets.

Environmental Effect on the Resolution of shf Lines.

While the solution of $CHCl_3$ or CH_2Cl_2 was polycrystalline by itself at 77 K, the mixed solution of $CHCl_3$–CH_2Cl_2 (1 : 1 volume ratio) exhibited an excellent glassy state when it was subjected to rapid cooling with liquid nitrogen. The shf lines observed in these different matrix states are compared in Fig. 5. It can clearly be seen from Fig. 5 that the mixed $CHCl_3$–CH_2Cl_2 solution gives no appreciable shf splittings, while both solutions show well-resolved shf lines.

It might be considered, therefore, that VOTPP molecules in the $CHCl_3$–CH_2Cl_2 glass have slightly different *g*-values and hf coupling constants, hence causing the apparent absence of shf splittings in the observed spectrum.

Triphenylphosphine formed an excellent glass at 77 K when the molten sample was subjected to sudden

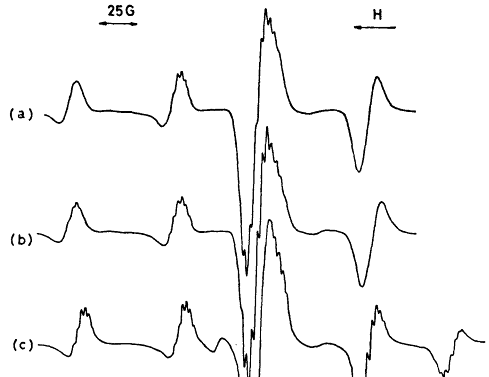

Fig. 4. Nitrogen shf splittings recorded for VOTPP diluted in some of the A-group matrices. (Only the central field portion of the spectra are reproduced in the figure.)
(a) Matrix: Toluene, [VOTPP]$=4.4\times10^{-3}$ M, $T=$ 77 K. (b) Matrix: Xylene (commercial mixture of the three isomeric xylenes), [VOTPP]$=4.4\times10^{-3}$ M, $T=77$ K. (c) Matrix: H_2TPP, Weight ratio of VOTPP/H_2TPP: about 1/200, $T=$room temp.

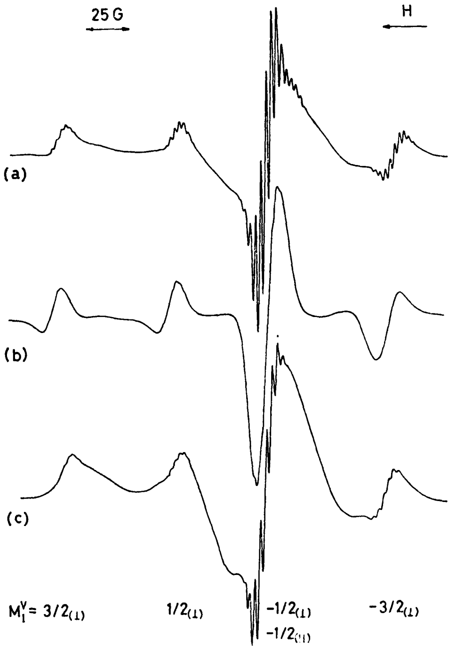

Fig. 5. Effect of matrix states on the resolution of nitrogen shf lines.
VOTPP diluted in the "polycrystalline" $CHCl_3$ matrix (a), in the "glassy" $CHCl_3$-CH_2Cl_2 (volume ratio, 1:1) matrix (b), and in the "polycrystalline" CH_2Cl_2 matrix (c). [VOTPP]$=2.9-3.2\times10^{-3}$ M, $T=77$ K.

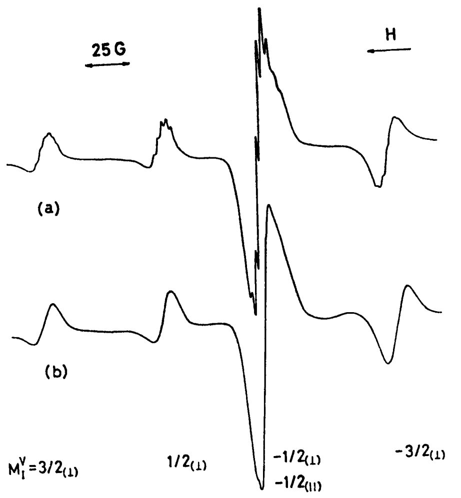

Fig. 6. Effect of matrix states on the resolution of nitrogen shf lines.
VOTPP diluted in the "polycrystalline" triphenylphosphine matrix (a) and in the "glassy" triphenylphosphine matrix (b). Weight ratio of VOTPP/triphenylphosphine: 1/250, T=77 K.

cooling with liquid nitrogen; the resulting glassy matrix was, however, converted into a polycrystalline one on warming to room temperature. Such a polycrystalline matrix was also formed upon cooling the molten triphenylphosphine slowly to room temperature. The ESR spectra obtained in these glassy and polycrystalline matrices are illustrated in Fig. 6, from which it can also be seen that the shf lines are resolved in the polycrystalline matrix rather than in the glassy one.

On the other hand, a commercial mixture of three isomeric xylenes was frozen in a glassy state at 77 K, each of the *o*-, *m*-, and *p*-xylenes was polycrystalline at 77 K. The order of the increasing resolution of the shf lines in these matrices was; xylene (mixture of the three isomers) > *o*-xylene $\simeq$ *m*-xylene > *p*-xylene. This is in marked contrast with the $CHCl_3$-CH_2Cl_2 systems.

For triphenylphosphate, both the glassy and polycrystalline samples were prepared in the same manner as triphenylphosphine. In this case, however, the resolution of the shf lines in the polycrystalline matrices was found to depend upon the method of sample preparation. When the polycrystalline matrix was prepared by cooling the molten triphenylphosphate to room temperature, the spectrum of VOTPP exhibited poorly-resolved hf lines without any shf splittings like that shown in Fig. 2. This indicates that the aggregation of VOTPP molecules takes place in the course of slow cooling. On the other hand, in the polycrystalline matrix obtained by warming the frozen glassy sample to room temperature, the shf lines were clearly detected. However, this spectrum changed from a well-resolved type into a poorly-resolved one with the lapse of time, suggesting that VOTPP molecules can diffuse through the polycrystalline triphenylphosphate matrix to form an aggregated state.

To summarize briefly, there is much evidence to show the importance of environments in the ESR spectra of VOTPP. A homogeneous dispersion of VOTPP molecules in a given matrix usually yields a highly-resolved spectrum. However, the method of obtaining such a dispersed state sensitively depends on the kind of matrix species and the mode of sample preparation.

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