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The Magnetic Properties of Verdazyl Free Radicals. VI. ESR Studies of Pairs and Triads† of the Symmetrical Triphenylverdazyl Radical in the 1,3,5-Triphenylbenzene Matrix

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Single-crystal ESR studies have been carried out on symmetrical triphenylverdazyl (TPV) doped in a diamagnetic 1,3,5-triphenylbenzene (TPB) crystal at room temperature. There have appeared seven pairs of fine-structure absorptions in addition to the hyperfine splittings. Three out of the seven pairs have been assigned as zero-field splittings due to radical pairs, while the other three pairs have been identified as from radical triads. The six fine structure tensors have been determined through the angular variation of the resonance-field separations. The structures of the pairs and triads of TPV were discussed on the basis of the fine structure tensors, the crystal structures of TPB and TPV, and the spin distribution in the radical molecule, assuming that the unit cell of the mixed crystal with the radical concentration of less than 11.1% is identical with that of the host crystal, TPB. Within the limits of the X-ray examination, this assumption was found to be reliable. It was found that the molecular planes in each species are almost parallel to the *bc*-plane and that all the *C*-phenyl rings lie in the *c*-direction.

Recently, the present authors have reported the temperature dependence of the ESR linewidth, the g-value shift, and the magnetic susceptibility of the powdered sample of symmetrical triphenylverdazyl (TPV) and have concluded from these data, the crystal structure, and the spin distribution that this radical solid is subjected to the magnetic phase-transition from the short-range ordered state to the long-range ordered one at about 1.7 K.[1,2] In order to clarify the magnetic properties of the TPV solid in more detail, single-crystal experiments are highly desirable. For this investigation, it would be a reasonable step to study the magnetic behavior of the radical pair or triad of TPV, since they are magnetic unit systems containing interacting spins. However, it is difficult in general to investigate precisely the magnetic dipolar and exchange interactions of the radical pair in the solid of the stable neutral radical at any temperature, because of the above interactions between the given two spins and the surrounding spins, which cause the work to be desperately complicated. In the rather fortunate case in which the species is defined well by some evidence, one can study the spin-spin interactions in the radical pair by making a certain portion of the radical diluted in a suitable diamagnetic crystal. This method is different from that employed in the case of the thermally-excited triplets[3] or the radical pairs caused by the irradiation.[4,5] In fact, the dilution method was applied to nitroxide radicals which possess a fairly localized electron spin.[6,7]

On the other hand, Wiersma and Kommandeur have pointed out that even a D-parameter depends largely upon the magnitude of the spin delocalization.[4] Therefore, it is also of particular interest to study the dipolar coupling tensor of a radical pair with delocalized spins and, in turn, to compare the tensor with that expected for the hypothetical radical pair with localized spins. The TPV radical not only has a delocalized spin,[1] by which its enormous stability can be understood, but its molecular structure is also well known,[8] so that this radical is an adequate example for the study of the effect of the spin delocalization on the magnetic properties.

By the way, the spin structure or the interaction between the spins and the lattice in the ordered state of TPV solid has not yet been made clear. For the purpose of clarifying this spin-lattice interaction, the study of the anisotropic dipolar interactions in the radical pair of TPV, its derivatives,[9] and its analogues[10] may be a possible approach, for the dipolar interaction Hamiltonian contains the scalar product of the spin and the vector distance, while the single-spin vector in the monoradical molecule has little interaction with the vector distance.

This paper will describe mainly the fine-structure tensors of the TPV radical pairs in the 1,3,5-triphenylbenzene (TPB) matrix in order to present the fundamental data for the above-mentioned studies as well as the investigation of these magnetic entities themselves. Besides, the possible TPV radical triads will also be discussed on the basis of the radical concentration, the ESR signal intensity, and the crystal structures of TPB and TPV.

The Crystal Structures of TPB and TPV. These structures were investigated by Farag[11] and Williams[8] respectively; they are shown in Figs. 1 and 2. It should be remarked that the molecular geometry of TPV is similar to that of TPB: Each configuration

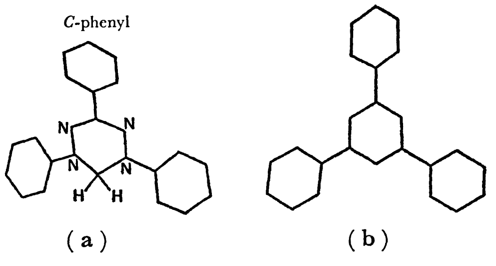

Fig. 1. Molecular structures of the TPV radical (a)[8] and diamagnetic TPB matrix (b).[11]

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† "Triad" means a three-membered radical cluster in which the exchange interaction energy should be much less than that of the ordinary chemical bond. We will refer to it as a "radical triad" in this text.

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of the three substituted phenyl rings of both the compounds is antipropellar in the crystalline state. Some molecular flexibility of the compounds may be encountered because of the bending and twisting freedom about the bonds connecting with the rigid ring systems. Furthermore, it should be noted that the large and intense diffused X-ray spots corresponding to thermal vibrations affecting the (200) planes of TPB signify that all the bonds in these planes are stronger than those normal to them[11] and that the elastic constant along the *a*-direction, which is almost normal to the molecular planes, as may be seen from Fig. 2, is naturally smaller than the others.[12] This fact may be favorable to accommodate the guest molecule, TPV, with a molecular thickness slightly different from that of the host molecule, TPB. In the meantime, Kuhn and Trischmann have reported a Debye-Scherrer X-ray photograph with sharp lines from the equi-molecular mixed crystal of TPB and TPV,[13] which may indicate a uniform mono-phase crystal. Therefore, it is expected, in the low-concentration region, that the guest molecules, TPV, can be doped substitutionally in the host, TPB, crystal without any drastical crystal distortion, as will be described in detail in a later section. Thus, the TPV molecules in the TPB matrix will be able to form radical pairs and triads with certain concentrations.

TPB is an orthorhombic crystal with the crystal parameters of $a=7.47$, $b=19.66$, $c=11.19$ Å, and $z=4$; the space group is $Pna2_1$.[11] The molecules inclined from the *bc*-plane by ±11° are stacked face-to-face and form two zigzag chains along the *a*-axis. The chains are related to each other by the twofold screw axis parallel to the *c*-axis. Since the interchain distance is longer than 10 Å, not only the nearest-neighboring but also the second-nearest-neighboring molecules can be found in the same chain, separated by 4.90 and 7.47 Å respectively. For the present purpose, it is safe to confine our consideration to one chain. The angle in the zigzag chain, which is bisected by the *bc*-plane, is about 100°, so that the radical pairs in the chain can be expected to be related to each other by the plane of symmetry parallel to the *bc*-plane. The most probable direction of the N–N bonds in the radical pair has been considered to be parallel to the *ac*-plane if the local symmetry around the radical pair is the same as that of the host crystal, since the crystal distortion of that orientation would be the smallest among those of the three possible orientations. The above arguments would also hold in the case of the radical triads.

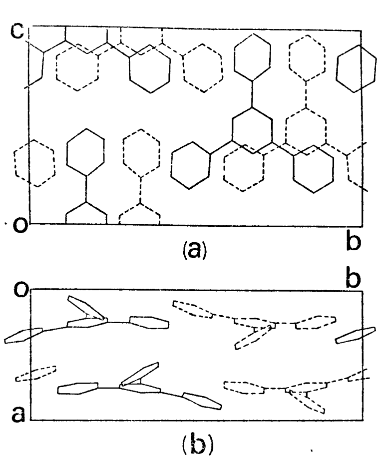

Fig. 2. Molecular packing of the host crystal, TPB.[11] (a) and (b) were projected along the crystallographic *a*- and *c*-axis, respectively.

Experimental

The TPV prepared by the method of Kuhn and Trischmann[13] was identified by the melting point, by studying the ESR spectrum in a solution, and by elementary analysis. The values obtained were in good agreement with those in the literature.[13] Commercial TPB was recrystallized from an ethereal solution; the results of the elementary analysis were satisfactory. The TPV and TPB (3 : 7 in weight) were dissolved together in an ether solvent and then slowly evaporated under nitrogen gas, thus giving small crystals. Then, the sample crystals of a suitable size were recrystallized again from the ethereal solution under a nitrogen gas flow for three days. Judging from the elementary analysis for carbon and nitrogen, the sample crystals contained TPV of 11.1% (Found: C, 92.15; N, 2.10%). More diluted crystals and reference crystals of pure TPB were also prepared by the same procedure.

The mixed and reference crystals were compared with each other, observing their crystal forms and cleavages, measuring their interfacial angles, and by the polarizing microscope technique. The X-ray diffraction spectra of the powdered samples were also compared with each other in the region from 7 to 40 degrees in 2θ, using Cu$K\alpha$ radiation.

The crystals used in the ESR measurements were mounted on the end of a synthesized polymer rod in various orientations by means of the goniometer. The ESR spectra about each of three mutually-perpendicular axes were obtained at room temperature by rotation at 5° intervals, using a JEOLCO JES-ME3X X-band spectrometer, equipped with a 100 kHz field modulation for the first derivatives and with an 80 Hz one for the second derivatives. The magnetic field was calibrated by the hyperfine splittings of Mn^{2+} in MgO.

The powdered sample containing 11.1% TPV exhibited the ESR absorptions characteristic of the randomly-oriented triplets. The half-field absorptions ($g=4$, $\Delta m_s=\pm 2$) were also observed in the powdered sample with a radical concentration of 11.1%, but no $\Delta m_s=\pm 2$ absorption was detected in the more diluted sample with a radical concentration of less than 3%.

Results and Spectral Analyses

Crystallography. When we compared the mixed crystals with the reference TPB crystals, no difference between them was detected, except for their colors, within the limits of our experimental error. This fact clearly indicates that the unit cell of the mixed crystal is identical macroscopically with that of the host crystal. Using the polarizing microscope, the samples were identified as single crystals. The sample crystal was of a trigonal form elongated along the *a*-axis and also showed an imperfect cleavage normal to that axis.[11] The faces parallel to the *a*-axis were (011) and $(01\bar{1})$ planes, and the interfacial angle was 59 degrees.

The mixed crystal with a radical concentration of less than 3% was studied by means of the ESR technique in order to clarify the orientation of the TPV molecules. For the rotation about the *a*-axis, the crystal exhibited a symmetrical single line with the small angular dependent peak-to-peak width of 12 gauss. For the rotation about the *b*- and *c*-axis, the resonance lines varied with the rotation of the crystal; the maximum number of the lines was 18, at which the over-all width of the resonance field spread to about 100 gauss. On the other hand, the ESR spectrum of TPV in solution gave nine lines with the hyperfine coupling constant of 6 gauss due to the almost-equivalent four nitrogen nuclei. These facts indicate that the angular dependent lines are attributable to the hyperfine splittings due to the nitrogen nuclei in the isolated radical, and that no radical oligomer has any significant population. It may also reasonably be deduced that this fairly planar π-radical can occupy at least two sites and that its molecular plane is nearly parallel to the *bc*-plane.

ESR Spectra. Figure 3 shows some typical ESR spectra of the 11.1% single crystal. The intense central peak in Fig. 3(A) and nine sharp peaks in Fig. 3(B) are due to the hyperfine interactions of the isolated radicals. Each of the absorption pairs with the resonance-field separation of d_{I} and $d_{\mathrm{I}'}$ in Fig. 3(A) is results from two differently-oriented species. The fine structure lines in Fig. 3(B) are broader than those in Fig. 3(A). Their linewidths, proportional to the over-all width of the central lines, are probably due to the hyperfine structure broadening, which indicates that the orientation of the molecules in the pairs and triads of TPV is similar to that of the isolated radicals.

The angular variations of the observed splittings denoted by d_{I}, d_{II}, *etc.* in Fig. 3 are shown in Fig. 4. The rectangular coordinate system a′b′c′ was chosen so as to avoid the overlap of the spectral lines in the orthorhombic crystal system *abc*. The relationship between the two right-hand systems is given by the following equation:

$$\begin{bmatrix} a \\ b \\ c \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{bmatrix} \begin{bmatrix} \mathrm{a}' \\ \mathrm{b}' \\ \mathrm{c}' \end{bmatrix}, \quad \alpha = -59.2^\circ \qquad (1)$$

where α is the angle measured from the *b*- to the b′-axis, equalling the interfacial angle between (011) and (01$\bar{1}$) planes.

Spectral Analysis of the Triplet. Under the conditions of (I) $g\beta H \gg |D|$, $|E|$ and (II) small g-anisotropy, the zero-field splittings of the triplet species can be analyzed by the approximate method described by Itoh.[14] Recently, this method has been successfully employed by Takizawa *et al.*[6] in the case of a radical pair in a matrix. The (I) assumption is considered to be valid in the present case, because the maximum value of the zero-field parameters is estimated to be less than 300 gauss from the angular variation of the splittings shown in Fig. 4. On the other hand, the g-values of the organic free radicals are usually almost isotropic and close to the free electron g-value. In fact, the g-value of TPV is found to be almost isotropic and to be very close to 2.0033. Therefore, the second assumption (II) is also reliable in the present case. We can thus introduce the following spin Hamiltonian:

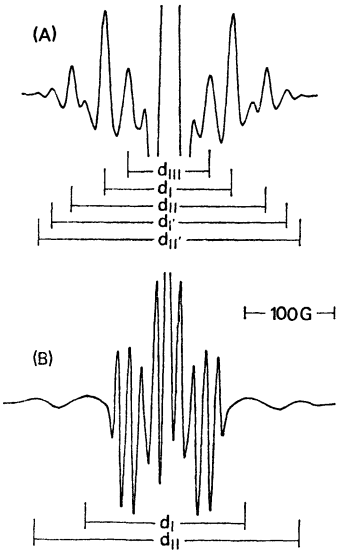

Fig. 3. Tracings of the ESR spectra from a single crystal of the diluted TPV radical. (A) $c /\!/ \mathbf{H}$, the second derivative; (B) $a /\!/ \mathbf{H}$, the second derivative.

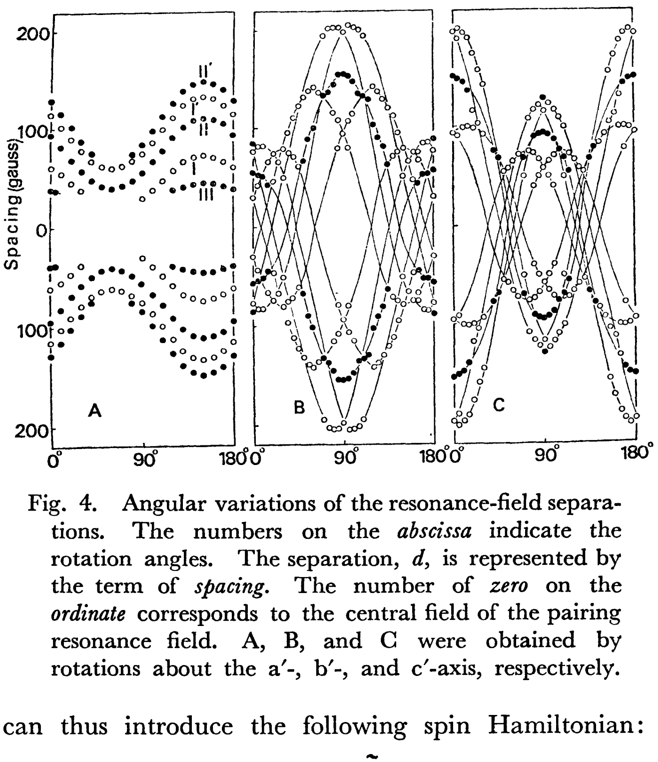

Fig. 4. Angular variations of the resonance-field separations. The numbers on the *abscissa* indicate the rotation angles. The separation, *d*, is represented by the term of *spacing*. The number of *zero* on the *ordinate* corresponds to the central field of the pairing resonance field. A, B, and C were obtained by rotations about the a′-, b′-, and c′-axis, respectively.

$$\mathrm{H} = g\beta\mathbf{S}\cdot\mathbf{H} + \mathbf{S}\cdot\tilde{\mathbf{D}}\cdot\mathbf{S}, \qquad (2)$$

where $\mathbf{S}=\mathbf{S}_1+\mathbf{S}_2$, and where the subscripts 1 and 2 indicate the respective radicals forming the radical pair. The other symbols have the usual meanings. The second term in Eq. (2) is the perturbing Hamiltonian. The second-order perturbation theory gives the following resonance-field separation of the doublet splitting in the case of a-axis rotation:

$$\begin{aligned} d &= 3(g_e/g)(D'_{zz}) \\ &= 3(g_e/g)(D'_{\mathrm{bb}}\cos^2\theta + D'_{\mathrm{bc}}\sin 2\theta + D'_{\mathrm{cc}}\sin^2\theta) \ \text{(gauss)}, \end{aligned} \qquad (3)$$

where g_e is the free electron g-value and where D'_{ij}

TABLE 1. OBSERVED FINE STRUCTURE TENSORS OF THE PAIRS AND TRIADS OF TPV RADICAL

Name	Principal values[a)]	Direction cosines with respect to *abc* system[b)]			D[c)] E[c)]
Radical pairs					
$\mathrm{I_a}$	±102.3	0.8550	0.5183	0.0182	153.5
	∓47.6	0.0617	−0.0667	−0.9959	3.5
	∓54.7	−0.5150	0.8526	−0.0891	
$\mathrm{I_b}$	±101.9	0.8543	−0.5196	−0.0149	152.8
	∓47.2	−0.0586	−0.0678	−0.9960	3.7
	∓54.6	0.5165	0.8517	−0.0884	
II	±99.4	0.9999	0.0046	0.0091	149.5
	∓74.2	0.0091	0.0118	−0.9999	24.5
	∓25.2	−0.0046	0.9999	0.0117	
Radical triads					
$\mathrm{I_a}'$	±66.9	0.9814	0.1920	−0.0017	100.3
	∓44.8	−0.0043	0.0127	−0.9999	11.4
	∓22.1	−0.1919	0.9814	0.0133	
$\mathrm{I_b}'$	±66.2	0.9863	−0.1605	0.0377	99.3
	∓45.1	0.0430	0.0298	−0.9987	12.0
	∓21.2	0.1591	0.9866	0.0364	
II′	±72.5	0.9999	−0.0044	0.0165	109.0
	∓49.8	0.0165	0.0016	−0.9999	13.5
	∓22.7	0.0043	1.0000	0.0015	

a) The alignment of the principal values is; D_{ZZ}, D_{XX}, and D_{YY}. The values were measured in gauss. Experimental errors in the values from $\mathrm{I_a}$ to $\mathrm{I_b}'$ were ±2.0 gauss. As for II′, an approximation which was described in the text was made. b) Experimental errors in directions were ±2°. c) The parameters were represented by an absolute value (in gauss).

(i,j=a, b, c) is the ij-component of the dipolar coupling tensor, $\tilde{\mathbf{D}}$, defined by the abc-system. The θ angle is measured from the b-axis to the external field, **H**. For the rotation about the other two axes, the separation, d, is also described by Eq. (3) with the cyclic replacement of the subscripts. By applying the least-squares method to Eq. (3), the components of the dipolar coupling tensor can be completely determined by means of the abc-system. Then, the resulting tensor is diagonalized, giving the principal values and their directions. The zero-field parameters are given by:

$$D = 3D_{\mathrm{ZZ}}/2 = D_{\mathrm{ZZ}} - (D_{\mathrm{XX}}+D_{\mathrm{YY}})/2,$$
$$E = (D_{\mathrm{XX}}-D_{\mathrm{YY}})/2, \tag{4}$$

where D_{KK} (K=X, Y, Z) represents the principal value. The results of the analysis are shown in Table 1.

Spectral Analysis of the Quartet. One can analyze the spectra due to the quartet state by the procedure employed in the case of the triplet state. As is well known, the spin Hamiltonian is given by Eq. (2), but $\mathbf{S}=\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3$, where the subscripts show the radicals in the radical triad. By employing the assumptions introduced in the last section and the second-order perturbation theory, the energy levels in terms of the Zeeman coordinate system, xyz, are obtained:

$$E(\pm 3/2) = (\pm 3/2)g\beta H + \varepsilon \pm \gamma,$$
$$E(\pm 1/2) = (\pm 1/2)g\beta H + \varepsilon' \pm \gamma',$$

where:

$$\varepsilon = (3/4)(3D_{zz}+D_{xx}+D_{yy}),$$
$$\varepsilon' = (1/4)\{D_{zz}+7(D_{xx}+D_{yy})\},$$
$$\gamma = \{24(D_{zx}{}^2+D_{yz}{}^2)+3(D_{xx}-D_{yy})^2+12D_{xy}{}^2\}/8g_{\mathrm{e}}\beta H,$$
$$\gamma' = \{-24(D_{zx}{}^2+D_{yz}{}^2)+3(D_{xx}-D_{yy})^2+12D_{xy}{}^2\}/8g_{\mathrm{e}}\beta H.$$

For the $\Delta m_{\mathrm{s}}=\pm 1$ transition, the three resonance fields are given by:

$$H(1/2-3/2) = (g_{\mathrm{e}}/g)(H_{\mathrm{o}}-\delta-\delta'),$$
$$H(-1/2-1/2) = (g_{\mathrm{e}}/g)(H_{\mathrm{o}}+\delta'') = (g_{\mathrm{e}}/g)H_{\mathrm{o}}(1+\delta''/H_{\mathrm{o}}), \tag{5}$$
$$H(-3/2- -1/2) = (g_{\mathrm{e}}/g)(H_{\mathrm{o}}+\delta-\delta'),$$

where:

$$\delta = 2D'_{zz} - (D'_{xx}+D'_{yy}),$$
$$\delta' = 6(D'_{zx}{}^2 + D'_{yz}{}^2)/H_{\mathrm{o}},$$
$$\delta'' = (3/4)\{8(D'_{zx}{}^2+D'_{yz}{}^2) - (D'_{xx}-D'_{yy})^2 - 4D'_{xy}{}^2\}/H_{\mathrm{o}}, \tag{6}$$

and where H_{o} stands for the resonance field of the free electron. The resonance-field separation, d, is as follows:

$$\begin{aligned} d &= H(-3/2- -1/2) - H(1/2-3/2) \\ &= 2(g_{\mathrm{e}}/g)(2D'_{zz}-D'_{xx}-D'_{yy}) \\ &= 6(g_{\mathrm{e}}/g)D'_{zz}, \end{aligned} \tag{7}$$

where we used this relationship: $D'_{xx}+D'_{yy}+D'_{zz}=0$. The $\tilde{\mathbf{D}}_{xyz}$-tensor in terms of the Zeeman coordinate system is represented by means of the $\tilde{\mathbf{D}}_{\mathrm{abc}}$-tensor, which is defined by the rectangular coordinate system fixed in a crystal, using a unitary matrix, $\tilde{\mathbf{U}}$:

$$\tilde{\mathbf{D}}_{xyz} = \tilde{\mathbf{U}}^{-1}\cdot\tilde{\mathbf{D}}_{\mathrm{abc}}\cdot\tilde{\mathbf{U}}. \tag{8}$$

When the crystal is rotated about the a-axis which coincides with the y-axis, and when the external field, **H**, makes an angle, θ, with the b-axis, $\tilde{\mathbf{U}}$ is represented by:

$$\tilde{\mathbf{U}} = \begin{bmatrix} 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \\ \cos\theta & 0 & \sin\theta \end{bmatrix}. \tag{9}$$

By using Eqs. (7)—(9), d is given by:

$$d = 6(g_{\mathrm{e}}/g)(D'_{\mathrm{bb}}\cos^2\theta+D'_{\mathrm{bc}}\sin 2\theta + D'_{\mathrm{cc}}\sin^2\theta). \tag{10}$$

Eq. (10) is similar to Eq. (3) used in the case of the triplet. Therefore, we can analyze the spectra due to the quartet state using Eq. (10), to which the same procedure as that employed in the last section is applied.

As for the (−1/2—1/2) transition, let us put the second-order term given by Eq. (6) on the far right-hand side in Eq. (5). The δ''/H_{o} ratio is estimated roughly to be 1/100 at most in the case of $H_{\mathrm{o}}=3000$, $D=200$ gauss, and $|E|<|D|$, so that the angular variation of the absorption is restricted within ±30 gauss from the central resonance field. Hence, the absorption is hard to detect in the radical triad in a matrix because of its overlap with the much more intense absorptions due to the isolated radicals.

The results of the analysis are also shown in Table 1, in which the indices from I to II′ correspond to the same subscripts and to the indices in Figs. 3 and 4 respectively. The subscripts, a and b, stand for the sites occupied by the radical oligomers. The directions obtained in the a′b′c′-system were transformed to those with respect to the orthorhombic one, *abc*, by using Eq. (1). In the case of the zero-field splitting, II′, we could measure $d_{\mathrm{II}'}$ only in two directions about the b′-axis and in only one about the c′-axis because of the quite weak absorption intensities in addition to the broader linewidths. However, the following approximation was taken based on the angular variations of the other splittings as well as the $d_{\mathrm{II}'}$ obtained: the absorption lines of II′ are overlapped with those of $\mathrm{I_a}'$ and $\mathrm{I_b}'$, at least in the vicinity of each summit in Figs. 4-B and 4-C. The directions obtained by such an approximation may be more reliable than the principal values.

Discussion

Discrimination of Radical Triad from Radical Pair. In the chain containing the radical molecules with a moderate concentration, **c**, the probabilities making the radical triad, the radical pair, and the isolated radical are $3\mathbf{c}^3(1-\mathbf{c})^2$, $2\mathbf{c}^2(1-\mathbf{c})^2$, and $\mathbf{c}(1-\mathbf{c})^2$ respectively. When **c** is 0.11, the ratios of the triad to the isolated radical and to the pair give 0.036 and 0.165 respectively. Therefore, the observation of the radical triad is possible by the usual ESR technique, using a rather bulky single crystal with a suitable radical concentration. The observed intensity ratio, $\Sigma I_{\mathrm{triad}}/\Sigma I_{\mathrm{pair}}$, is about 0.12 after the correction for the absorption from the $(-1/2$—$1/2)$ transition. This value is quite close to the calculated one, provided that the signal intensities are proportional to the concentrations of the species along with a common proportionality constant.†† This result supports our assignment of the radical oligomers. Other evidence for the identification will be discussed later.*

Structure of the Radical Pair. The $\tilde{\mathbf{D}}$-tensors of $\mathrm{I_a}$ and $\mathrm{I_b}$ satisfy the aforementioned symmetry within the limits of experimental error. The angles between the *a*-axis and each z-axis in these radical pairs are both 31°, which is close to the angle of 40° deduced from the intrachain angle of the host crystal. The $\tilde{\mathbf{D}}$-tensors, $\mathrm{I_a}$ and $\mathrm{I_b}$, can, therefore, be attributed to the radical pairs which are formed from the TPV molecules located as nearest-neighbors to each other in the host crystal. On the other hand, the x-axis coincides approximately with the *c*-axis. This implies that one of the substituted phenyl rings is almost in the *c*-direction; this is consistent with the crystal structure of TPB, in view of the molecular geometry of TPV. However, we can not definitely decide the orientation of the *C*-phenyl rings (see Fig. 1) on the basis of the $\tilde{\mathbf{D}}$-tensor alone, as will be discussed in later section.

The *D*-parameter of II is the same as those of $\mathrm{I_a}$ and $\mathrm{I_b}$, but the three principal axes coincide with the orthorhombic crystal axes within the limits of experimental error. The absorption intensity ratio of $I_{\mathrm{II}}/I_{\mathrm{I_a}}$ is about 3/4. These results were reproduced using another sample of a (1 : 4) mixture, so this species is an intrinsic radical pair in the TPV-TPB system. The structure of this radical pair, based on the $\tilde{\mathbf{D}}$-tensor, is as follows: both of the molecular planes in this pair are parallel to the *bc*-plane, and the *C*-phenyl rings are in the *c*-direction; the second molecule is just above the first molecule, the distance between them being about *a*/2. This structure implies that the molecules in this pair have; (i) a planar geometry or (ii) a plane of symmetry. The first possibility, (i), is alternative evidence for the planar geometry of the TPV molecule, although Williams has revealed it by means of X-ray diffraction.[8] As for the second possibility, (ii), we would like to present the following facts: the symmetrically-substituted verdazyls seem to possess a plane of symmetry in their crystalline state.** In fact, TPV itself has a pseudo- or almost-mirror plane.[8]***

Radical Triad. The $\tilde{\mathbf{D}}$-tensors of $\mathrm{I_a}'$ and $\mathrm{I_b}'$ in Table 1 have the same symmetry as that of the tensors of $\mathrm{I_a}$ and $\mathrm{I_b}$ within the limits of experimental error. The *a*-axis and each of the z-axes in the former make angles of 10°, which is one-third of that in the latter. The above results suggest that the $\tilde{\mathbf{D}}$-tensors of $\mathrm{I_a}'$ and $\mathrm{I_b}'$ ought to be attributed to the radical triads. If it were not for the radical triad, one should presume another radical pair with an intermolecular distance less than that of the pair, $\mathrm{I_a}$, without the third radical molecule on either side of the latter pair causing the deformation of the pair. A similar comment can be made on the $\mathrm{I_b}$ and II radical pairs. On the other hand, the directions of the $\tilde{\mathbf{D}}$-tensor, II′, are also similar to those of the tensor, II. The tensor of II′ can also be attributed to the radical triad for the same reason. All the results may be consistent with the structures of the radical triads proposed in Fig. 5; each triad is formed by adding one radical molecule to each aforementioned radical pair to the position obtained by the *a*-transla-

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†† When both the electron-spin-exchange interactions in the radical oligomers are antiferromagnetic, and when a linear alignment of the spins in the radical triad is taken, the more reasonable signal intensity ratio, $I_{\mathrm{triad}}/I_{\mathrm{pair}}$ $(=r)$, can be given by:

$$\begin{aligned} r &= 3\mathbf{c}^3(1-\mathbf{c})^2\chi_{\mathrm{q}}\{2\mathbf{c}^2(1-\mathbf{c})^2\chi_{\mathrm{t}}\}^{-1} \\ &= 15\mathbf{c}\{3+\exp(2|J_{\mathrm{t}}|/kT)\}[8\{2+\exp(3|J_{\mathrm{q}}|/2kT) \\ &\qquad +\exp(5|J_{\mathrm{q}}|/2kT)\}]^{-1}, \end{aligned}$$

where χ_{q} and χ_{t} are the magnetic susceptibilities due to the quartet and triplet states respectively. J_{q} and J_{t} stand for the exchange integrals in the radical triad and the pair respectively. *T* and *k* have the usual meanings. When one puts $\mathbf{c}=0.11$, $T=300$ K, and $-J_{\mathrm{q}}/k=-J_{\mathrm{t}}/k=10$, 50, 100 K into the equation, the ratios give 0.203, 0.189, and 0.172 respectively. The exchange integrals, $|J/k|$'s, in the present radical oligomers are supposed to be from ten to a few score degrees. Therefore, the approximation $(r=3\mathbf{c}^3(1-\mathbf{c})^2/2\mathbf{c}^2(1-\mathbf{c})^2$ $(=0.165$ for $\mathbf{c}=0.11))$ mentioned in the text is considered to be a tolerable one.

* The possibility of the observation of the radical tetrad was not discussed, because the ratio of the tetrad to the triad is about 1/10.

** Two symmetrical verdazyls have a plane of symmetry (Ref. 15).

*** Note that Fig. 1(a) was not projected along the normal of the molecular plane.

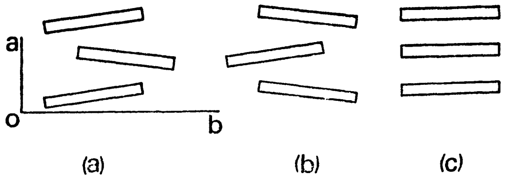

Fig. 5. Schematic drawings of chemical structures of the proposed radical triads projected along the *c*-axis. (a), (b), and (c) correspond to the radical triads I_a', I_b', and II′, respectively. Oblongs stand for the sections of the idealized molecular planes.

tion of that occupied by the first molecule in the pair.

The absorption-intensity ratio, $I_{II'}/(I_{I_a'}+I_{I_b'})$, is very close to the $I_{II}/(I_{I_a}+I_{I_b})$ ratio. This suggests the following mechanism for the formation of the radical oligomer in the TPV-TPB system. There are two types of positions occupied by the first radical molecule; (A) one is one of the four general positions determined originally by the host molecules in the unit cell, and (B) the other is a special one. The positions occupied by one kind of radical oligomer are all of the same type, that is, A-A or B-B and A-A-A or B-B-B for the radical pairs and triads respectively. This mechanism also may explain the observation of only three $\tilde{\mathbf{D}}$-tensors for the radical triads. The letters correspond to the subscripts in Table 1. On the basis of the above consideration, we expect that the B-B-B type stacking may be a meta-stable packing of the host and the guest molecules. Actually, a molecular packing very similar to this type has been found in the 1,3,5-triphenyl-6-methylverdazyl crystal.[15)]

The spin multiplicity of the fine structure defined by the resonance-field separation, d_{III}, is not clear at present, although the signal intensity can be explained well by assuming a radical triad containing one TPB molecule in its structure rather than presuming a second-nearest-neighboring radical pair.

$\tilde{D}$-Tensor Calculation with Spin Densities. The calculation of the dipolar coupling tensors of the proposed radical pairs is made in order to clarify the orientation of the *C*-phenyl rings in the pairs and in order to examine the effect of the spin delocalization on the $\tilde{\mathbf{D}}$-tensor. The parameters, *D* and *E*, of radical pairs have already been calculated by several authors[4,16)] on the basis of the molecular orbital theory. Although the present method is essentially the same as theirs, the principal values and their directions are both obtained by our method. The spin Hamiltonian which is considered to be valid for the radical pair is given by:

$$\mathrm{H_D} = \sum_{i,j} g^2\beta^2\rho_i\rho_j\{\mathbf{S}_1\cdot\mathbf{S}_2/r_{ij}^3-3(\mathbf{S}_1\cdot\mathbf{r}_{ij})(\mathbf{S}_2\cdot\mathbf{r}_{ij})/r_{ij}^5\}, \qquad (11)$$

where ρ_i and ρ_j are the π-spin densities on the *i* atom in the first molecule, 1, and on the *j* atom in the second molecule, 2, and where $\mathbf{r}_{ij}$ is the vector distance connecting *i* to *j*. The Hamiltonian, Eq. (11), is rewritten in a matrix form by means of the total spin, $\mathbf{S}=\mathbf{S}_1+\mathbf{S}_2$:

$$\mathrm{H_D} = \mathbf{S}\cdot\tilde{\mathbf{D}}\cdot\mathbf{S},$$

where the symmetrical tensor is:

$$\tilde{\mathbf{D}} = \begin{bmatrix} D_{\mathrm{xx}} & D_{\mathrm{xy}} & D_{\mathrm{xz}} \\ D_{\mathrm{xy}} & D_{\mathrm{yy}} & D_{\mathrm{yz}} \\ D_{\mathrm{xz}} & D_{\mathrm{yz}} & D_{\mathrm{zz}} \end{bmatrix}, \qquad (12)$$

and where:

$$D_{\mathrm{mm}} = (1/2)g^2\beta^2\sum_{i,j}\rho_i\rho_j(r_{ij}^2-3\mathrm{m}_{ij}^2)/r_{ij}^5, \quad (\mathrm{m=x, y, z}),$$

$$D_{\mathrm{mn}} = (1/2)g^2\beta^2\sum_{i,j}\rho_i\rho_j(-3\mathrm{m}_{ij}\mathrm{n}_{ij})/r_{ij}^5,$$

$$(\mathrm{m, n=x, y, z;\ but\ m\neq n}).$$

The $\tilde{\mathbf{D}}$-tensor given by Eq. (12) can be calculated in an arbitrary rectangular coordinate system if the structure of the radical pair and the spin distribution are known, followed by diagonalization. However, we use an alternative method in which the Zeeman system is employed and in which only the *zz*-component is used:

$$\begin{aligned} D'_{zz} &= (1/2)g\beta\sum_{i,j}\rho_i\rho_j(r_{ij}^2-3z_{ij}^2)/r_{ij}^5 \\ &= (1/2)g\beta\sum_{i,j}\rho_i\rho_j(1-3\cos^2\theta_{ij})/r_{ij}^3, \end{aligned} \qquad (13)$$

where θ_{ij} is the angle between the vector, $\mathbf{r}_{ij}$, and an applied field, **H**. Putting Eq. (13) into Eq. (3), we obtain:

$$d = (3/2)g_e\beta\sum_{i,j}\rho_i\rho_j(1-3\cos^2\theta_{ij})/r_{ij}^3, \qquad (14)$$

By employing Eq. (14), the diagonalized $\tilde{\mathbf{D}}$-tensor is obtained by the procedure described in the section on spectral analyses.

The results of the calculation are shown in Table 2, together with the directions of the *C*-phenyl rings. When the calculation was carried out, the spin densities were taken from Ref. 1. The vector distances were deduced from the host crystal for the I_1 and I_2 radical pairs. As for the II_1 and II_2 pairs, the distances have been estimated from the structures in which the first molecules are the same as those in the I_1 and I_2 pairs, while the second molecules are obtained by the *a*/2-translation of the first molecules. In the table, the $\tilde{\mathbf{D}}$-tensor of I_a in Table 1 is close to the I_1 rather than to the I_2. This result suggests that the *C*-phenyl rings in the I_a and I_b radical pairs are in the *c*-direction, which is consistent with our expectation. II_1 also explains II; this indicates again the orientation of the *C*-phenyl rings in the radical pair of II along the *c*-axis. The discrepancy between the observed and the calculated $\tilde{\mathbf{D}}$-tensors depends mainly on the difference between the true and the presumed vector distances. However, the results of the calculation may not only support our assignment of the radical pairs with the proposed structure, but also suggest that the $\tilde{\mathbf{D}}$-tensors due to the proposed radical triads can not be explained by assuming the radical pairs with *C*-phenyl rings differently oriented from those in the I_a, I_b, and II pairs.

In order to compare the *D*-parameters observed and calculated above with that expected from a point-spin approach, we estimated the latter to be 240 gauss by using the relation: $D=(3/2)g\beta/r^3$.[17)] On the other hand, the *D*-parameters observed and calculated by our method are 150 and 130 gauss respectively. This

TABLE 2. CALCULATED DIPOLAR COUPLING TENSORS OF THE PROPOSED RADICAL PAIRS

Name[a)]	Principal values[d)]	Direction cosines with respect to *abc* system			D[e)] E[e)]
I_1	±85.5	0.9065	0.4219	0.0142	128.2
	∓49.2	−0.0249	0.0199	0.9995	6.5
	∓36.3	−0.4214	0.9064	−0.0285	
I_2[b)]	±68.1	0.7638	0.6430	0.0557	102.2
	∓39.2	−0.6173	0.7530	−0.2277	5.2
	∓28.9	−0.1884	0.1396	0.9721	
II_1	±120.3	0.9989	0.0432	0.0168	180.4
	∓73.6	−0.0171	0.0079	0.9998	13.5
	∓46.6	−0.0430	0.9990	−0.0086	
II_2[c)]	±119.4	0.9967	0.0359	0.0728	179.2
	∓72.2	0.0048	0.8699	−0.4932	12.5
	∓47.2	−0.0811	0.4919	0.8669	

a) The capital letters correspond to those in Table 1. I_1 and II_1; *C*-phenyl rings are in the *c*-direction. b) An alternative candidate for radical pair I_a; the respective *C*-phenyl rings lie in the [011] and [01$\bar{1}$] directions. c) Another candidate for radical pair II; the *C*-phenyl rings lie in the [01$\bar{1}$] direction. d) The order of the principal values is the same as that in Table 1. The values were measured in gauss. e) Refer to the last footnote in Table 1.

large discrepancy of 90 gauss may indicate that the point-spin approach to the radical pair with the delocalized spins is a very rough approximation.

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