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Electron Spin Resonance of 2,2′-Bipyridyl, Dimethyl-2,2′-Bipyridyls, and 2,2′-Biquinolyl in their Phosphorescent Triplet States

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Electron spin resonance (ESR) of phosphorescent triplet states of 2,2′-bipyridyl, 3,3′-, 4,4′-, 5,5′-, and 6,6′-dimethyl-2,2′-bipyridyls, and 2,2′-biquinolyl has been studied in ethanol glasses. For 2,2′-bipyridyl, the ESR spectrum of both the *E* and *Z* conformers was observed in poly(vinyl alcohol) films and their assignment was examined by changing the direction of applied magnetic field. Using such a technique, the stretched polymer-film method has been developed for determining the molecular conformations which are difficult to be estimated from zero-field splitting (ZFS) parameters obtained in rigid glasses. As a result, the conformations in the phosphorescent triplet states of molecules studied here are confirmed to be all *E* in ethanol glasses, even for a case with a relatively small *E* value.

2,2′-Bipyridyl (BPY)[†] is one of typical bidentate ligands which are coordinated with many metal ions in the *Z* conformation. In the solutions or in the crystal, however, the ground state of the molecule is in the *E* conformation,[1,2] although the structure may not perfectly be planar. As a result, the *Z* conformer of free BPY has not conclusively been identified in any kind of experiments. Recently, we have succeeded in observing two sets of electron spin resonance (ESR) signals which are originated from the *Z* and *E* conformers in the phosphorescent triplet state when the molecules were dissolved in poly(vinyl alcohol) (PVA) films.[3,4] For the phosphorescent triplet states of symmetrically substituted dimethyl-2,2′-bipyridyls (DMBPY's)[†] and 2,2′-biquinolyl (BQL)[†], the conformations are also expected to be *E* but any experimental evidence for it has not yet been reported. In the present work, therefore, a further ESR study of these molecules in ethanol glasses was carried out, in connection with their conformations. In this case, we have developed a new technique for determining the *Z* and *E* conformations of paramagnetic species by applying the stretched polymer-film method.

In the triplet state of molecules, the magnetic fine structure may well be explained by the following spin Hamiltonian:

$$\begin{aligned}\mathscr{H} &= g\mu_{\rm B}\boldsymbol{B}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\boldsymbol{D}\cdot\boldsymbol{S} \\ &= g\mu_{\rm B}\boldsymbol{B}\cdot\boldsymbol{S} - XS_x^2 - YS_y^2 - ZS_z^2 \\ &= g\mu_{\rm B}\boldsymbol{B}\cdot\boldsymbol{S} + D[S_z^2-(1/3)S(S+1)] + E[S_x^2-S_y^2] \\ &\qquad (S=1).\end{aligned}$$

Here, $\boldsymbol{D}$ is the fine structure tensor with principal values of $-X$, $-Y$, and $-Z$, and D and E are the zero-field splitting (ZFS) parameters. The other symbols have their usual meaning and the anisotropy of g was disregarded. Assuming a planar structure of molecule in the phosphorescent triplet state, the coordinate axes were taken as follows: the principal magnetic axes, x and y, are in the molecular plane (the x axis is taken rather close to the long direction of molecule), while the z axis is perpendicular to the molecular plane.

In *Z* conformers of BPY's (or BQL), the x axis is taken to be parallel to the central C–C bond which connects the two pyridine (or quinoline) rings (hereafter, we will refer to such a direction as b), while that of *E* conformers should be separated to the b in direction by some angle of $\alpha_{\rm x}(0<|\alpha_{\rm x}|<\pi/4)$. Such a difference on the direction of magnetic axis is certainly important for determining the conformation of molecules studied here.

Application of Stretched Polymer-Film Method for Determining Conformations

Only from the ESR spectrum observed in a rigid glass, the assignment of each peak is directly impossible and information about the conformation of the molecule studied is not easily obtainable. For symmetrically substituted biphenyls, bipyridyls, and related compounds, the molecular structures in the phosphorescent triplet state may in general be nearly planar, because of the increase of bond order in the central C–C bond which connects two of the same aromatic rings. For the *Z* conformers with symmetry C_{2v}, one of the principal axes of the $\boldsymbol{D}$ tensor, say x axis, should be parallel to this bond (x||b), while for the *E* conformers with symmetry C_{2h} the x axis is in a direction separated from b by $\alpha_{\rm x}$. When the magnetic induction $\boldsymbol{B}$ is applied parallel to one of the principal magnetic axes, the peak intensity at the corresponding resonance field is maximum in regularly oriented molecular assembly. These relations make possible to determine the conformation of these molecules by applying the stretched polymer-film method following the procedure described below.

When a PVA film containing appropriate amount of molecules to be studied is stretched more than 200% of stretch, we have already confirmed that these molecules are partially oriented with the following tendency: (1) the molecular plane is difficult to be oriented perpendicular to the stretched direction (s); (2) the long molecular axis has a tendency to align to the s direction; (3) the molecular plane is preferably oriented parallel to the film plane. From such a stretched film, we made several kinds of narrow oblong strips, the

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[†] In the present paper, 2,2′-bipyridyl, dimethyl-2,2′-bipyridyl, and 2,2′-biquinolyl are abbreviated as BPY, DMBPY, and BQL, respectively.

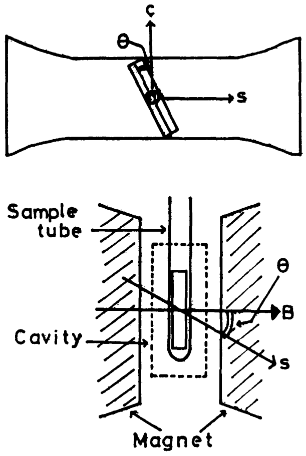

Fig. 1. Coordinate system in stretched PVA films, and the narrow oblong strips used in ESR measurements.

long sides of which were cut at various angles θ''s with direction c which is perpendicular to s in the film plane, as shown in Fig. 1. When several sheets of such strips with the same θ are inserted and fixed in the same direction in the sample tube in the cavity, their s direction makes an angle of θ with $\boldsymbol{B}$ which is applied in the film plane. We will designate an angle between the principal magnetic x axis and the s direction as θ_X. Actually, the line shape of the ESR spectrum changes from the case with $\theta=\theta_X$ by using the strips with another angle of θ.

If the guest molecules are oriented in perfect ordering as in a single crystal, the intensities of the X peaks should be maximum when $\theta=\theta_X$ where the x axis is placed parallel to $\boldsymbol{B}$ (hereafter, we will refer to an angle giving the maximum intensity as θ_M). Although the molecules dissolved in stretched PVA films are partially oriented, the peak intensity decreases if the direction of $\boldsymbol{B}$ deviates from that of the principal magnetic axes. This means that the maximum intensity of each peak should be observed at $\theta_M \approx \theta_X$, even if the line shapes are generally broad in PVA films as compared with the case of a single crystal. As a result, we can reasonably distinguish the *E* conformer with $\theta_X \neq 0$ from the *Z* conformer with $\theta_X=0$, except the case when the θ_X of the *E* conformer is nearly zero. For *E* conformers in stretched polymer films, there are two types of orientations where the principal magnetic axes make angles $\pm\theta_X$ with the s direction even in an ideal alignment. Consequently, the X peak of the *E* conformer may be rather broad as compared with that of the *Z* conformer if the former θ_X is fairly small. Therefore, we may pertinently assign the conformation as follows: a peak with $\theta_X \neq 0$ and/or with relatively broad line shape generally arises from the *E* conformer, whereas that with $\theta_M=0$ and with relatively sharp line shape is attributed to the *Z* conformer.

Experimental

The ESR measurements were carried out for BPY, 3,3'-, 4,4'-, 5,5'-, and 6,6'-DMBPY's and BQL in ethanol glasses. A purified sample of 3,3'-DMBPY used was donated by Dr. H. M. Suzuki (Government Industrial Research Institute, Tohoku, Nigatake), and purified 4,4'- and 5,5'-DMBPY's were donated by Dr. Y. Kaizu (Tokyo Institute of Technology). All the other compounds were purchased from Tokyo Kasei Co.. BPY and BQL were purified by recrystallization, but DMBPY's were used without further purification.

In determining the conformation of some of these molecules, PVA films containing its appropriate amount were prepared by either the solution-evaporating method[3] or the diffusion-penetrating method.[4] In the case of BPY, the former method was used, that is, after mixing of an aqueous solution of PVA with an ethanol solution of BPY, a film with 2×10^{-2} cm thick was obtained by evaporating solutions on a glass plate. On the other hand, the latter method was used for 5,5'-DMBPY and BQL because of their insolubility in water, that is, a pure PVA film with 2×10^{-2} cm thick was made on a glass plate by evaporating water from the aqueous solution. After heat treatment for about an hour at 80 °C and swelling in water for about three hours at 30 °C, the film was soaked in methanol solution of a sample until its appropriate amount was penetrated into the film by diffusion. Then, the film thus prepared by either of the methods was stretched for about five minutes at about 60 °C. The obtained stretched films are about 7×10^{-3} cm thick, and with about 250% of stretch in the s direction and about 30% of contraction in the c direction.

For the ESR measurement, a sample tube containing ethanol solution with appropriate concentration of a compound was set in a quartz dewar with fingertip which was inserted in the cavity. The ESR spectra were observed at 77 K using JEOL JES-ME-3X spectrometer with 100 kHz modulation at microwave frequencies close to 9.2 GHz and the applied $\boldsymbol{B}$ between 0.1 and 0.5 T. The microwave field was perpendicular to $\boldsymbol{B}$ and the microwave frequency was measured with a cavity frequency meter. The magnetic induction was calibrated with a proton magnetic resonance technique. The exciting light was provided by a 500 W super-pressure mercury arc lamp filtered through 5 cm of distilled water and a Toshiba UV-31 or UV-D25 filter.

In the case of 3,3'-DMBPY, the observed ESR signals were considerably weak and accumulated by using a signal averager (1024 channel Kawasaki Electronica TM-1610S) for improving the signal to noise ratios in the following way: appropriate times of scans were accumulated with the exciting light on and the same times of scans were subtracted with the light off. In this way, we obtained a spectrum without perceptible baseline drifts which were due to signals of free radicals produced by UV irradiation and of magnetic contaminants in the cavity.

Results

In ethanol glasses, all the X, Y, and Z peaks for the $\Delta m=\pm1$ transitions of the phosphorescent molecules studied here were clearly observed as shown in Figs. 2 and 3, except the Y and Z signals of 3,3'-DMBPY and the high-field Y peak of BQL shown in Fig. 4. Accordingly, the *Y* and *Z* values of 3,3'-DMBPY were estimated from the resonance fields of X component and the trace-less relation of $\boldsymbol{D}$ tensor. The *X*, *Y*, and *Z* values of the other BPY's were directly obtained from the corresponding set of resonance fields. Since the observed resonance fields of DMBPY's did not significantly deviate from those of (*E*)-BPY, they were assigned to be in the same ordering of magnitude as those of (*E*)-BPY. For BQL, however, the assignment of the resonance fields has not yet been performed.[5] Therefore,

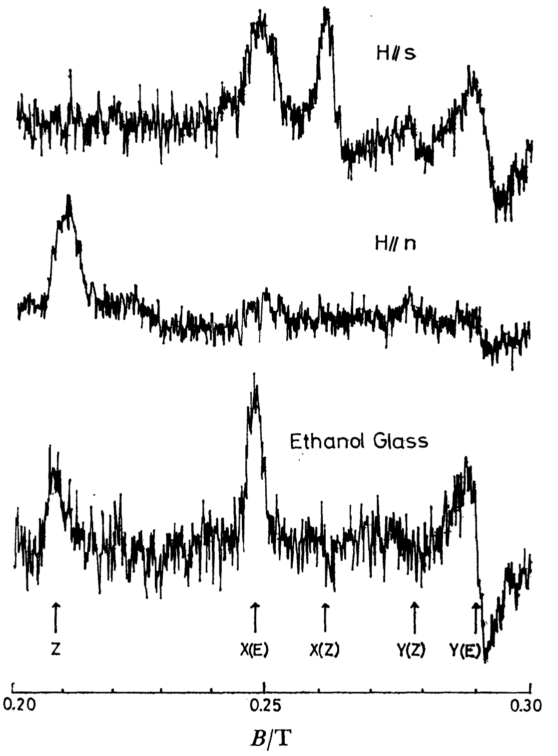

Fig. 2. ESR spectra of the low field $\Delta m = \pm 1$ transitions for the phosphorescent triplet state of (Z)- and (E)-2,2′-bipyridyl in a stretched PVA film and in ethanol glass at 77 K.

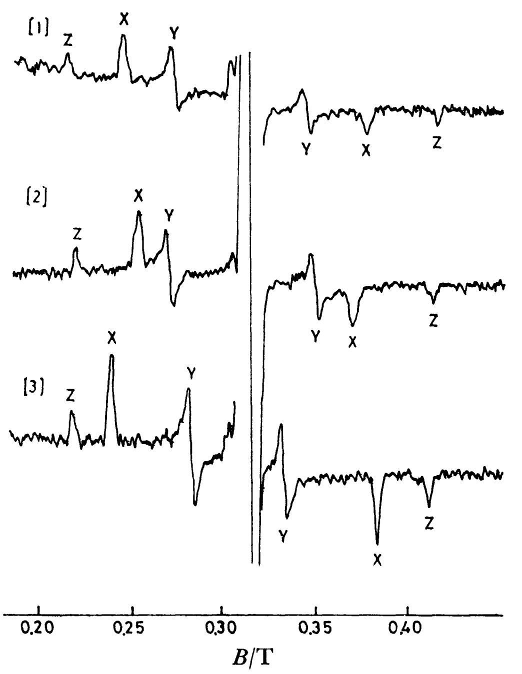

Fig. 3. ESR spectra of the $\Delta m = \pm 1$ transitions for the phosphorescent triplet states of 4,4′-dimethyl-2,2′-bipyridyl (1), 5,5′-dimethyl-2,2′-bipyridyl (2), and 6,6′-dimethyl-2,2′-bipyridyl (3) in ethanol glasses at 77 K.

we have carried out it by using the stretched polymer-film method[3,4] with reference to Fig. 4. The ZFS parameters thus obtained are listed in Table 1.

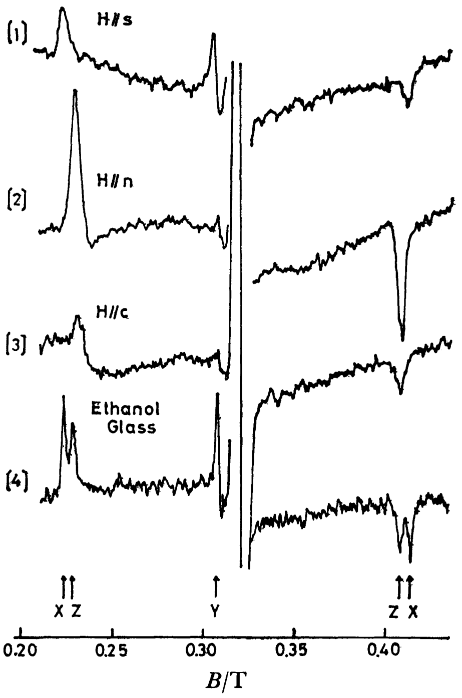

Fig. 4. ESR spectra of the $\Delta m = \pm 1$ transitions for the phosphorescent triplet state of 2,2′-biquinolyl in stretched PVA films (1—3), and in ethanol glass (4) at 77 K.

ESR measurements for the phosphorescent triplet state of BPY have already been carried out in rigid glasses[5,7] or in stretched PVA films.[3,4] Especially in the latter case, we observed two sets of X and Y peaks and one set of Z peaks for the $\Delta m = \pm 1$ transitions as shown in Fig. 2. When $B \| s$, the intensities of the X and Y peaks which can be observed in ethanol glasses are not much different from each other, but the other X peaks are relatively enhanced as compared with the other Y peaks. As a result, we have reasonably concluded that the former set of signals is pertinent to the E conformer and the latter to the Z conformer, since $\theta_X = 0$ for the Z conformer while $\theta_X \neq 0$ for the E conformer.

Under these circumstances, we have tried to determine these conformation by applying the technique described previously. First, we prepared narrow oblong strips of the stretched BPY-containing PVA films with various θ. The ESR measurements were carried out for these samples under irradiation. In this case, the intensities of X peaks for the Z and E conformers, $I_X(Z)$ and $I_X(E)$, respectively, were actually changed by using a sample with different value of θ, while that of Z peaks, I_Z, should not be varied if the strips prepared from the identical stretched film were used under the same condition of electromagnetic field in the cavity. Plotting the relative intensities of $I_X(Z)/I_Z$ and $I_X(E)/I_Z$, we found $\theta_M = 0°$ and $\theta_M \approx 5°$ for the Z and the E conformer, respectively, although the variation of $I_X(E)/I_Z$ is relatively gentle near θ_M as compared with that of $I_X(Z)/I_Z$. This may apparently imply the facts that the previous conclusion is exactly correct and that the stretched polymer-film technique is actually available for determing the conformation of molecules even if only one set of peaks were observed. The ZFS para-

TABLE 1. ZERO-FIELD SPLITTING PARAMETERS IN THE PHOSPHORESCENT TRIPLET STATES (cm^{-1})

Molecule	Host	$\lvert X\rvert/hc$	$\lvert Y\rvert/hc$	$\lvert Z\rvert/hc$	$\lvert D\rvert/hc$	$\lvert E\rvert/hc$	D^*/hc[a]	D^*/hc[b]
(*Z*)-2,2′-Bipyridyl	PVA film	0.0416	0.0327	0.0723	0.1094	0.0045	0.1097	0.1105
(*E*)-2,2′-Bipyridyl	EtOH glass	0.0487	0.0246	0.0737	0.1104	0.0121	0.1124	0.1121
	PVA film	0.0489	0.0242	0.0723	0.1089	0.0123	0.1110	0.1105
(*E*)-3,3′-Dimethyl-2,2′-bipyridyl	EtOH glass	0.0479	(0.019)	(0.067)	0.101	0.014	0.104	0.1052
(*E*)-4,4′-Dimethyl-2,2′-bipyridyl	EtOH glass	0.0475	0.0257	0.0732	0.1098	0.0109	0.1114	0.1109
(*E*)-5,5′-Dimethyl-2,2′-bipyridyl	EtOH glass	0.0418	0.0287	0.0705	0.1057	0.0066	0.1063	0.1070
	PVA film	0.0410	0.0291	0.0701	0.1051	0.0060	0.1056	0.1046
(*E*)-6,6′-Dimethyl-2,2′-bipyridyl	EtOH glass	0.0520	0.0178	0.0703	0.1052	0.0171	0.1093	0.1090
(*E*)-2,2′-Biquinolyl	EtOH glass	0.0699	(0.0037)	0.0662	0.0992	0.0368	0.1179	0.1178
	PVA film	0.0672	(0.0032)	0.0640	0.0960	0.0352	0.1137	0.1134

a) $D^*=(D^2+3E^2)^{1/2}$. b) Obtained from the observed resonance field of the $\Delta m=\pm 2$ transition with Kottis-Lefebvre's correction.[6]

meters obtained in the stretched PVA films are also given in Table 1.

For 3,3′-DMBPY, the *Z*-conformer should not be planar because of the steric hindrance between the two methyl groups. In such a case, the *D* value may be fairly large as compared with the planar (*Z*)-BPY by considering the result of phosphorescent 2,2′-dimethylbiphenyl by Scheve and Wagner.[8] Since the *D* value obtained is rather small as compared with that of BPY, one may reasonably infer that 3,3′-DMBPY observed in the present work is actually the *E* conformer.

4,4′- and 6,6′-DMBPY's are *meta*-methyl-substituents to the carbon 2 (and 2′) which is bonded to another pyridine ring. In these cases, the electronic structures may not be much different from that of BPY, and the *D* and *E* values of each conformer are expected to be relatively close to those by BPY with the same conformation. In the present result, the *D* and *E* values obtained for these molecules are rather close to those of (*E*)-BPY than those of (*Z*)-BPY. This may suggest the fact that the ZFS parameters of 4,4′- and 6,6′-DMBPY's listed in Table 1 are apparently those of the *E* conformers.

For 5,5′-DMBPY, the obtained *D* and *E* values appear to be close to those of (*Z*)-BPY rather than those of (*E*)-BPY. However, the molecule is a *para*-methyl-substituent to the carbon 2 (and 2′), and the influence of substitution to the electronic structure may not be very small. Further, all the other BPY's observed here are *E* conformers in ethanol glasses. Considering these facts, we have applied the stretched polymer-film technique for determining the conformation of the molecule. The experimental procedure adopted was quite the same as in the case of BPY. The resonance fields were scarcely changed from the case of ethanol glasses if the microwave frequency was kept nearly the same, and no new peak was detected. This is a quite different situation from the case of BPY where the peaks of both the *Z* and *E* conformers were observed. Then the relative intensity I_X/I_Z was plotted against θ and its maximum value was found at $\theta_M \approx 5°$. This may imply that 5,5′-DMBPY observed was the *E* conformer, inspite of its relatively small *E* value.

In the phosphorescent triplet state of BQL, the conformation has not conclusively been determined, although the possibility of *E* was discussed by Rabold and Piette.[5] For determining the conformation, therefore, experiments similar with those of 5,5′-DMBPY were carried out using the stretched BQL-containing PVA films. The resonance fields were almost unchanged from the case of ethanol glasses if the microwave frequency was kept nearly the same, and no new peak was observed. In this case, we have found a small peak for relative intensity of I_X/I_Z near $\theta_M \approx 15°$, although its variation is very gentle. This may possibly suggest the fact that the conformation of BQL detected here is also *E* as in its ground state.

Discussion

Applying the stretched polymer-film technique, we have succeeded in assigning the conformation of BPY's and BQL in the phosphorescent triplet state. As a further study, we leave some possibility to proceed for determining the direction of principal magnetic axes by improving the present procedure. In the present study, however, such a work was not undertaken, since the molecules studied here are rather reactive with the environments in the excited state and the ESR signals decrease rapidly during UV irradiation. For the purpose of such a determination, therefore, it may be desirable to choose a set of guest compound and host polymer which are stable with each other under irradiation. In this case, the analysis may actually become easier in the use of a stretched polymer film with better alignment of guest molecules, such as a stretched film without contraction in the c direction.[9] However, one should remember that there are two types of orientations with $\pm\theta_X$ for *E* conformers in stretched polymer films, even in an ideal alignment of guest molecules. Especially when the $|\theta_X|$ is small and/or when the *Z* conformers exist together with the *E* conformers with a small $|\theta_X|$, these ESR peaks may become overlapped with each other. As a result, one should analyze the ESR line shape by a satisfactory computer simulation using a distribution function with orthorhombic character.

In the present work, we have confirmed that the stable conformations of BPY, 3,3′-, 4,4′-, 5,5′-, and 6,6′-DMBPY's and BQL in the phosphorescent triplet state are all *E* in ethanol glasses. This is a quite natural conclusion in consideration of the intramolecular steric interactions for the *Z* and *E* conformations, similar with those in the ground state. In these molecules, the *D* and *E* values have not hitherto been determined except for the case of BPY, although the D^* values of 4,4′- and 5,5′-DMBPY's10) and BQL5) have already been reported.

Among DMBPY's, the *E* values listed in Table 1 are fairly different from each other, whereas the change of the *D* values is relatively small. Such a difference of *E* values may be rather complicated because of the superposition of the change of spin distribution caused by the nitrogen heteroatom upon that by the substitution of another pyridine ring. As a result, the conformation of these molecules is generally difficult to determine merely from the magnitude of *E* value when only one of the conformers was detected.

In examining the trend of the ZFS parameter to the spin distribution, the *E* values of these molecules were simply evaluated from the lowest triplet configuration, in which one electron is excited from the highest occupied orbital ϕ^{ho} of the ground state to the lowest vacant orbital ϕ^{lv}. Using the simple LCAO-MO's with Streitwieser's parameters,11) the spin densities at each atom, ρ^{ho} and ρ^{lv}, which originate from the singly occupied orbitals of ϕ^{ho} and ϕ^{lv}, respectively, were separately obtained within McLachlan's approximation.12) Then the *E* values were roughly estimated from these spin densities by including only interactions between the neighboring atoms. In this calculation, the molecules were assumed to be planar, all the bond lengths and bond angles were taken the values of the ground state of benzene molecule,13) and the electron spin dipoles were assumed to be located at each nucleus with the above spin distributions. In fact, such a treatment may be allowed to estimate in-plane components of the **D** tensor.

TABLE 2. *E*/*hc* VALUES OF 2,2′-BIPYRIDYLS CALCULATED FROM THE SPIN DENSITIES OF SINGLY OCCUPIED ORBITALS (cm^{-1})

	$E(Z)_{\mathrm{calcd}}/hc$	$E(E)_{\mathrm{calcd}}/hc$	$[E(E)_{\mathrm{obsd}}-E(E)_{\mathrm{calcd}}]/hc$a)
2,2′-Bipyridyl	0.0089	0.0106	0.0015
3,3′-Dimethyl-2,2′-bipyridyl	0.0142	0.0161	−0.002
4,4′-Dimethyl-2,2′-bipyridyl	0.0059	0.0097	0.0012
5,5′-Dimethyl-2,2′-bipyridyl	0.0089	0.0089	−0.0023
6,6′-Dimethyl-2,2′-bipyridyl	0.0097	0.0158	0.0013

a) $E(E)_{\mathrm{obsd}}$'s are the values observed in ethanol glasses.

As given in Table 2, the result thus obtained is in qualitative agreement with the experimental one except that the *E* value of 3,3′-DMBPY is slightly larger than that of 6,6′-DMBPY. Such a qualitative agreement may imply that the difference among the *E* values is mainly due to the change of spin distribution arising from the methyl position in each pyridine ring. As the overestimation of *E* value for 3,3′-DMBPY is actually small, this discrepancy may possibly be due to the formation of hydrogen-bond between the nitrogen atom and one of the methyl protons. It may be noted here that if the spin density of the triplet state at each atom $\rho_i=(\rho_i^{\mathrm{lv}}+\rho_i^{\mathrm{ho}})/2$ is used in such an evaluation only a qualitative trend for the *E* values cannot satisfactorily be obtained, since the ZFS originates from the interaction between two different electron spins. Actually, the present evaluation should be applicable to a comparison among molecules with similar structures because of its simplicity.

If the a axis is taken to be perpendicular to the b direction (parallel to the central C–C bond) in the molecular plane of BPY or symmetrically substituted BPY's, the off-diagonal component of the **D** tensor, $(3/4)g^2\mu_{\mathrm{B}}{}^2\langle -2\mathrm{ba}/\mathrm{r}^5\rangle$, is non-zero for the *E* conformer, while it is zero for the *Z* conformer. So far as the simple LCAO-MO's are used for the evaluation of spin distribution, the other components of $(3/4)g^2\mu_{\mathrm{B}}{}^2\langle(\mathrm{r}^2-3\mathrm{z}^2)/\mathrm{r}^5\rangle$ and $(3/4)g^2\mu_{\mathrm{B}}{}^2\langle(\mathrm{a}^2-\mathrm{b}^2)/\mathrm{r}^5\rangle$ of the *E* conformer are unchanged from those of the corresponding *Z* conformer. As a result, one may roughly infer that the *E* value of the *Z* conformer is generally small as compared with that of the corresponding *E* conformer, while the *D* values in these conformations are nearly the same, as in the case of BPY. It may be noted here that such a relation should not be valid for cases where the higher order effects on the spin distribution are not very small and there are exceptions for some of the related molecules. For example, the *E* value of (*Z*)-dimethylbiphenyls is rather larger than that of the corresponding *E* conformer, although the difference between them is relatively small.8)

Since the point-dipole approximation is less satisfactory to the out-of-plane component in the **D** tensor, the *D* values were not evaluated in the present work. A more detailed calculation of the ZFS parameters will be published in the forthcoming paper.

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