The Conformers of 2,2′-Bipyridine in the Phosphorescent Triplet State as Studied by Electron Spin Resonance and Phosphorescence

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(Received July 19, 1984)

Two sets of triplet-state ESR spectra corresponding to the *s-cis* and *s-trans* conformers of 2,2′-bipyridine have been observed in mixtures of water with various alcohols at 77K. The intensity ratio of the ESR signal for the *s-cis* conformer to that for the *s-trans* conformer depends on the composition of the mixture and on the sample-cooling rate. From the analysis of the phosphorescence spectra, the lowest triplet state of the *s-cis* conformer is estimated to be close to that of the *s-trans* conformer. An anomalous ESR signal which cannot be ascribed to either the *s-cis* conformer or the *s-trans* conformer has been observed in a 1-propanol-water mixture. The geometries of these conformers are discussed from their observed zero-field splitting parameters, together with their potential energy diagrams, as obtained by an *ab initio* calculation.

2,2′-Bipyridine (BPY) is a typical chelating agent for metal ions. The photophysics and photochemistry of complexes of BPY are under active investigation, with particular interest being taken in their application to solar-energy-conversion schemes. The *s-cis* and *s-trans* conformations are possible in BPY, as is shown in Fig. 1. The ground-state molecule has the *s-trans* conformation in solutions[1-3] or in the crystalline state.[4] The excited-state molecule also has the *s-trans* conformation in rigid solutions at low temperatures.[5] Although the *s-cis* conformer of free BPY was not observed until a few years ago, the chelated *s-cis* conformer undoubtedly exists in the metal-chelate compounds of BPY.[6-8]

Recently, we have succeeded, by using a poly(vinyl alcohol) (PVA) film as a host, in finding two sets of ESR spectra originating from the *s-cis* and *s-trans* conformers in the phosphorescent triplet states.[9,10] In rigid solutions, however, the triplet state BPY has for many years been considered to be in the *s-trans* conformation. In the present work, we have observed two sets of triplet-state ESR spectra of free BPY using mixtures of water with various alcohols (methanol, 1-propanol, 2-propanol, ethylene glycol, 1,2-propanediol, 1,3-propanediol, and glycerol) as rigid solvents.

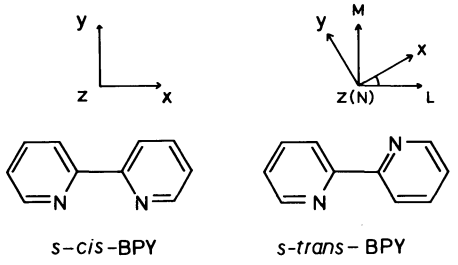

Fig. 1. Molecular structures and coordinate systems chosen for *s-cis*- and *s-trans*-2,2′-bipyridines.

The magnetic fine structure in an external magnetic field $\boldsymbol{B}$ can be described by the spin Hamiltonian:

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

Here, D is the zero-field splitting (ZFS) tensor with principal values of $-X$, $-Y$, and $-Z$, and D and E are the ZFS parameters. In the present work, the anisotropy of the g-tensor was neglected. Assuming a planar structure of the molecule in the phosphorescent triplet state, the coordinate axes were taken to be as shown in Fig. 1. For *s-cis*-BPY with the C_{2v} symmetry, the x axis is taken to be parallel to the central carbon–carbon bond which connects the two pyridine rings (hereafter, we will refer to such a direction as L), while for *s-trans*-BPY with the C_{2h} symmetry, the x axis should not be parallel to the direction L. Using such a difference in the direction of the principal axes of the ZFS tensor relative to the molecular axes, the two sets of X and Y peaks observed in the stretched PVA film were assigned as is shown in Fig. 2c.[10]

Experimental

The 2,2′-bipyridine (Aldrich) was purified by sublimation *in vacuo*. 1-Propanol (Tokyo Kasei G. R. Grade) was purified by distillation. The methanol (Dotite Spectrosol), 2-propanol (Dotite Spectrosol), ethylene glycol (Tokyo Kasei G. R. Grade), 1,2-propanediol (Tokyo Kasei G. R. Grade), 1,3-propanediol (Tokyo Kasei E. P. Grade), and glycerol (Wako Spectrosol) were used without further purification. The solvent mixtures were checked for the absence of an extraneous ESR signal prior to use. The solutions of BPY were prepared at the concentration of 3×10^{-3} mol dm^{-3}.

For the ESR measurements, the excitations were carried out using a Canrad-Hanovia 1 kW Xe-Hg lamp through a Toshiba UV-D33S glass filter, 5 cm of distilled water, and a Copal DC-495 electromechanical shutter. The decays of the ESR signals were measured by using a 1024-channel Kawasaki Electronica TM-1610S signal-averager system. The details of the ESR measurements were essentially the same as those reported previously.[10]

For the phosphorescence measurements, the excitations were done by the use of an Ushio USH-500D 500W mercury-arc lamp equipped with the glass filter mentioned above. The emissions from a sample were passed through a Jobin-Yvon HR-1000 monochromator and detected by means of a Hamamatsu Photonics R453 photomultiplier tube. All the measurements were carried out at 77K.

Results and Discussion

The ESR spectra of the phosphorescent triplet state of BPY were measured in ethanol and methanol-water (MeOH-H_2O) mixtures at 77K. The observed ESR spectra of the low-field $\Delta m_S=1$ transitions are shown in Fig. 2. For comparison, Fig. 2c shows the ESR spectrum observed in a stretched PVA film when the applied magnetic field $\boldsymbol{B}$ is parallel to the stretched direction s.

In the MeOH-H_2O mixtures, two sets of X and Y peaks and one set of Z peaks were observed, while in the ethanol solution only one set of X, Y, and Z peaks was observed. The X and Y peaks which can not be observed in the ethanol solution can reasonably be assigned to the *s-cis* conformer, for their resonance fields are almost the same as those for the *s-cis* conformer observed in the stretched PVA film. The ZFS parameters obtained are listed in Table 1.

The X and Y peaks assigned to the *s-cis* conformer of free BPY should not be attributed to signals from the complex with Zn^{2+}, which results from the contamination of polar solvents with traces of Zn^{2+}. The reasons for this assignment are as follows: (1) The ZFS parameters of the *s-cis* conformer are different from those of the Zn^{2+} complex, as is shown in Table 1; (2) the observed phosphorescence lifetime of the *s-cis* conformer in MeOH-H_2O (4:1 by volume) at 77K is 0.97s, while that of the Zn^{2+} complex is 1.16 s in the same solvent at the same temperature; (3) the intensity ratio of X peaks for the *s-cis* conformer to those for the *s-trans* conformer decreases as the MeOH content increases above 35wt% of MeOH, as is shown in Fig. 3. The last phenomenon suggests that the two sets of ESR

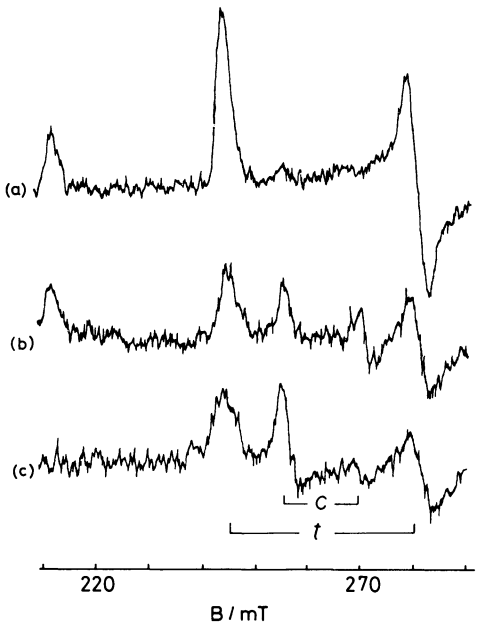

Fig. 2. ESR spectra of the low-field $\Delta m_S=1$ transitions for the phosphorescent triplet state of 2,2'-bipyridine at 77K. (a): In ethanol, (b): in MeOH-H_2O (3:1 by volume), (c): in a stretched PVA film with $\boldsymbol{B}$//s.

Table 1. ZFS parameters and lifetimes, τ, in the phosphorescent triplet states at 77 K

Molecule	Host	$\lvert X\rvert$ / cm^{-1}	$\lvert Y\rvert$ / cm^{-1}	$\lvert Z\rvert$ / cm^{-1}	$\lvert D\rvert$ / cm^{-1}	$\lvert E\rvert$ / cm^{-1}	D^{*} [a] / cm^{-1}	τ / s
s-trans-BPY	Ethanol	0.0487	0.0246	0.0737	0.1104	0.0121	0.1121	0.96
	PVA	0.0482	0.0237	0.0719[b]	0.1079	0.0123	0.1100	—
	MeOH-H_2O[c]	0.0479	0.0242	0.0722[b]	0.1081	0.0119	0.1102	0.97
	n-PrOH-H_2O[d]	0.0486	0.0242	0.0728[b]	0.1092	0.0122	0.1157	0.95
s-cis-BPY	PVA	0.0411	0.0317	0.0727[b]	0.1091	0.0047	0.1100	—
	MeOH-H_2O[c]	0.0411	0.0312	0.0723[b]	0.1084	0.0050	0.1102	0.97
	n-PrOH-H_2O[d]	0.0416	0.0316	0.0732[b]	0.1098	0.0050	0.1157	0.96
A-BPY	*n*-PrOH-H_2O[d]	0.0384	0.0317	0.0701[b]	0.1051	0.0033	—	0.94
B-BPY	*n*-PrOH-H_2O[d]	—	—	—	—	—	—	0.94
$[Zn(bpy)]^{2+}$	MeOH-H_2O[e]	0.0418	0.0306	0.0724	0.1087	0.0056	0.1090	1.16

a) Obtained from the observed resonance field of the $\Delta m_S=2$ transition with Kottis-Lefebvre's correction.[22] b) Obtained from X and Y by using the $X+Y+Z=0$ relation. c) MeOH-H_2O (4:1 by volume). d) *n*-PrOH-H_2O (35wt% of *n*-PrOH). e) Solutions of the complexes were prepared by the addition of $Zn(NO_3)_2$ (3×10^{-2} mol dm^{-3}) and free BPY (3×10^{-3} mol dm^{-3}) to the MeOH-H_2O (4:1 by volume) solution.

spectra should not be attributed to the formation of aggregates of BPY in MeOH–H_2O mixtures.

The intensities of the X peaks for the *s-cis* and *s-trans* conformers, $I_X(c)$ and $I_X(t)$ respectively, were measured as a function of the weight percentage of MeOH. The results are shown in Fig. 3. The $I_X(c)/\{I_X(c)+I_X(t)\}$ value increases with an increase in the amount of MeOH and gives a maximum at about 35wt% of MeOH.

In 1-propanol-water (*n*-PrOH–H_2O) mixtures, the situation is more complex. As is shown in Fig. 3, only one set of ESR signals corresponding to the *s-trans* conformer was observed in the *n*-PrOH–H_2O mixtures below 22wt% of *n*-PrOH. In the range from 23 to 29wt% of *n*-PrOH, the relative intensity of the X peaks for the *s-cis* conformer to those for the *s-trans* conformer increases with an increase in the amount of *n*-PrOH. In the range from 32 to 36wt% of *n*-PrOH, only one set of X peaks corresponding to the *s-cis* conformer was observed. As can clearly be seen in Fig. 3, there is a distinct discontinuity at 37wt% of *n*-PrOH. In the range from 38 to 100wt% of *n*-PrOH, only one set of the *s-trans* conformer signals was observed. At present we can not find the reason for the discontinuity observed at 37wt% of *n*-PrOH. However, it should be noted that, at 37wt% of *n*-PrOH, the mixed solvent forms a clear glass with a low cracking frequency and that the $\Delta m_S=1$ signals are too weak to be observed because of the very fast photochemical decomposition.

In *n*-PrOH–H_2O mixtures, the intensity ratio of the ESR signal for the *s-cis* conformer to that for the *s-trans* conformer depends on the sample-cooling rate. The results presented above were obtained with rapidly frozen samples. The sample-cooling rate was controlled by changing the penetration rate of a quartz sample tube (5 mm o.d.) into liquid nitrogen. In this experiment, the penetration rate could be changed between 2.5 and 300mm/min. In mixtures of 35wt% of *n*-PrOH, only one set of the *s-cis*-conformer signals was observed from rapidly frozen samples, while only one set of the *s-trans*-conformer signals was observed from slowly frozen samples. As is shown in Fig. 4c, two sets of the ESR signals which are not ascribed to the *s-cis* or *s-trans* conformer were observed for the samples precooled in the following manner: The bottom of the sample tube was placed in contact with the surface of liquid nitrogen for at least 10 min and then immersed in liquid nitrogen. The conformer which gives the relatively strong ESR signals at 260.1 and 270.8 mT will hereafter be denoted as the *A* conformer, while the conformer which gives the weak ESR signal at 265.7 mT will hereafter be denoted as the *B* conformer. On the other hand, the ESR signal at about 212 mT is broad and shows no structure. Although the conformation of the *A* conformer seems to be unclear, the ZFS pattern for this conformer may be assumed to be the same as those for the *s-cis* and *s-trans* conformers. The ZFS parameters thus obtained are listed in Table 1. The ZFS parameters of the *B* conformer was difficult to obtain because of its weak ESR signals. The phosphorescence lifetimes obtained from the decay of the ESR $\Delta m_S=1$ transition signal are also listed in Table 1. It is difficult to separate the observed ESR spectra into four component spectra by using a time-resolved technique because they have almost the same phosphorescence lifetime.

The *D* values of the *s-cis* and *s-trans* conformers are nearly the same, while that of the *A* conformer is smaller than those of these conformers. So long as the simple LCAO-MO's are used for the evaluation of spin distribution, however, one may roughly infer that the *D* values of the planar *s-cis* and *s-trans* conformers are nearly the same, this is in accord with the experimental results.[10] On the other hand, a preliminary π electron calculation made in our laboratory suggests that the *D* value of biphenyl becomes smaller by twisting

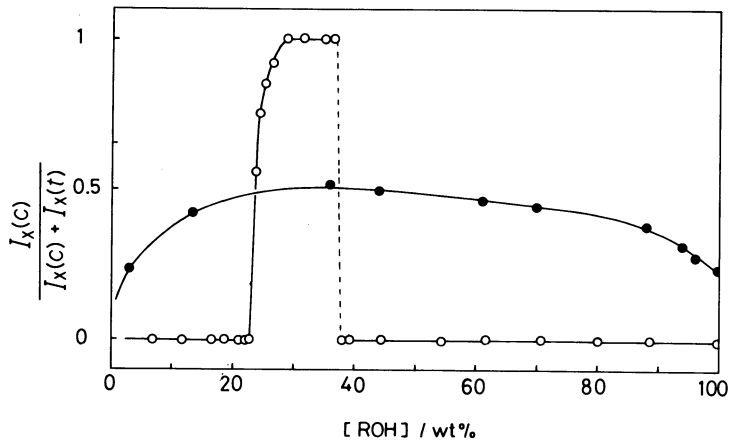

Fig. 3. Plots of $I_X(c)/\{I_X(c)+I_X(t)\}$ *versus* the weight percentage of MeOH and *n*-PrOH.
●: MeOH, ○: *n*-PrOH.

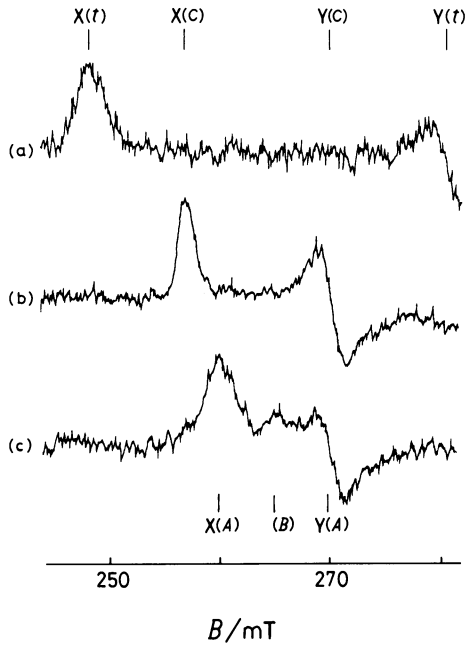

Fig. 4. ESR spectra of the low-field $\Delta m_S = 1$ transitions for the phosphorescent triplet state of 2,2-bipyridine in *n*-PrOH–H_2O (35wt % of *n*-PrOH) at 77K. (a): For the slowly frozen sample, (b): for the rapidly frozen sample, (c): for the precooled sample.

around the inter-ring bond. As a result, it may be deduced that the *A* conformer has a nonplanar triplet state. In order to discuss the conformations of the lower electronic states more thoroughly, an *ab initio* calculation with a STO-3G basis set[11] was carried out for BPY, changing its inter-ring angle. At first, the optimized geometries of planar *s-cis*- and *s-trans*-BPY, with symmetries of C_{2v} and C_{2h} respectively, were determined by using the energy-gradient method.[12] The bond lengths and the bond angles thus obtained are shown in Fig. 5. When the geometry of each pyridine ring is maintained the same as in the *s-trans*-BPY, as given in Fig. 5, the SCF-MO's of the lowest-energy state were calculated by rotating the pyridine rings around the central single bond, C_2–$C_{2'}$. Using these SCF-MO's, the excitation energies of the lower electronic states were evaluated, including interactions among configurations which arise from one of the six highest occupied MO's to one of the four lowest unoccupied MO's in the ground state. The potential energy diagrams of BPY thus obtained are shown in Fig. 6.

The energy curve of the ground state (^{1}A) shown in Fig. 6 is nearly the same as that reported by Agresti *et al.*, in which the geometry of each pyridine ring was the same as the experimental one of *s-trans*-BPY.[13,14] In the present SCF-MO calculation, the geometry-optimized energy of the planar *s-cis* conformer obtained is 0.277 eV high in energy compared with that of the *s-trans* conformer. Therefore, the energy of the ground state near θ=180° can be expected to be lowered somewhat compared with that shown in Fig. 6. The lowest triplet state (^{3}B) is most stable at θ=0°, and its energy curve is, in general, similar to that of biphenyl as obtained semiempirically by Imamura and Hoffmann.[15] On the other hand, the highest and the second highest occupied orbitals, and also the lowest and the second lowest unoccupied orbitals in the ground state, both degenerate at an angle of twist near θ=90°. In this region, therefore, the second excited triplet state (^{3}A) is most stable and is located close to the lowest triplet state (^{3}B), as is shown in Fig. 6. As a result, the spin distributions and the ZFS parameters of these states may not differ much from each other

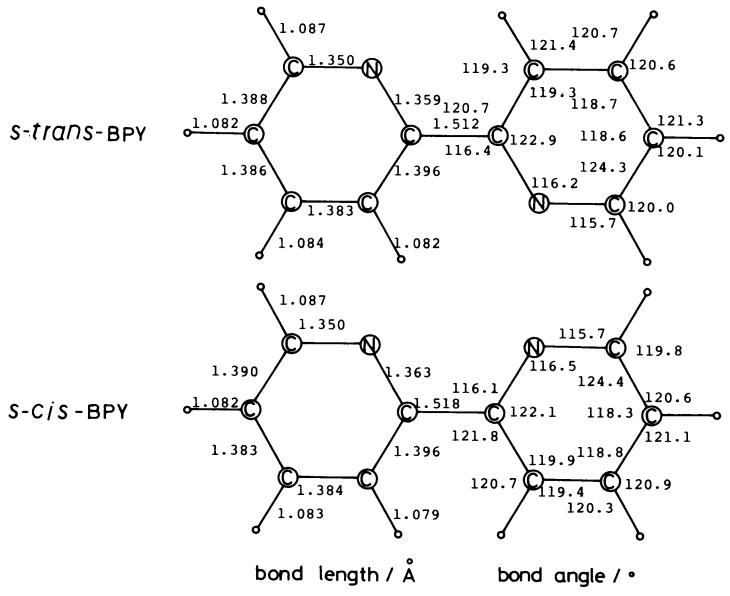

Fig. 5. Optimized geometries of *s-cis*- and *s-trans*-2,2'-bipyridines.

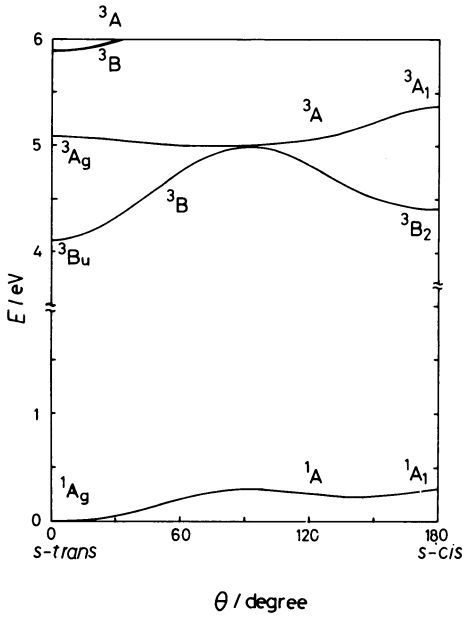

Fig. 6. Potential energy diagrams of 2,2'-bipyridine as a function of the angle of twist θ between the pyridine rings.

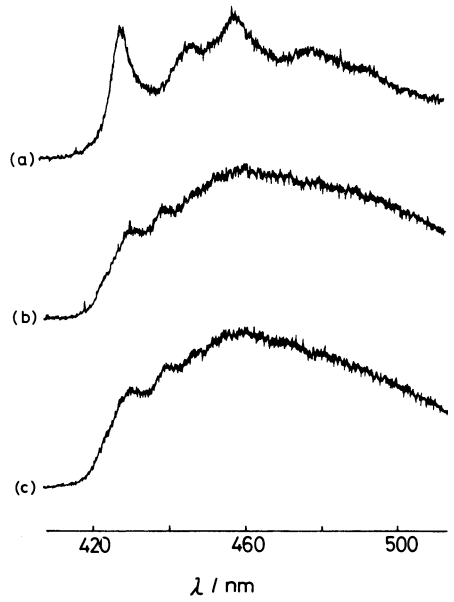

Fig. 7. Phosphorescence spectra of 2,2'-bipyridine in *n*-PrOH–H_2O (35wt % of *n*-PrOH) at 77K. (a): For the slowly frozen sample, (b): for the rapidly frozen sample, (c): for the precooled sample.

near θ=90°. Such a tendency may not be essentially changed if the approximations adopted are improved. Although the *A* conformer is most probably the nonplanar ^{3}B state, there remains another possibility that the *A* or *B* conformer is the ^{3}A state, if this state becomes the lowest excited triplet state near θ=90° under the influence of the medium. In the present work, however, a more detailed calculation of the triplet-state geometry with the intermolecular interaction was not carried out.

The phosphorescence spectra of BPY were measured in *n*-PrOH–H_2O (35wt% of *n*-PrOH) when the samples were cooled under the same conditions as in the ESR measurements. The results are shown in Fig. 7. When those results are compared with those of the ESR measurements, the phosphorescence spectra shown in Figs. 7a, 7b, and 7c may be interpreted as due to the *s-trans*, *s-cis*, and *A* and *B* conformers respectively. The phosphorescence spectrum shown in Fig. 7a is similar to that observed in ethanol at 90K.[16] The phosphorescence spectra of the *A* and *B* conformers (Fig. 7c) are almost the same as that of the *s-cis* conformer (Fig. 7b). The lineshape of the phosphorescence spectrum of the *s-trans* conformer is sharper than that of the *s-cis* conformer, while the lineshape of the ESR spectrum of the *s-trans* conformer is broader than that of the *s-cis* conformer. Although the phosphorescence spectra of the *s-cis*, *A*, and *B* conformers can not be exactly observed because of their broadness, the lowest triplet states of these conformers are estimated to be close to that of the *s-trans* conformer, 23400 cm^{-1}.

The ESR spectra of the *s-cis* and *s-trans* conformers were measured in MeOH–H_2O (4:1 by volume) with

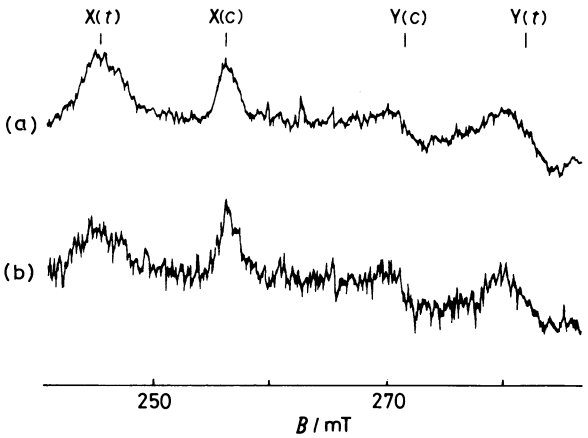

Fig. 8. ESR spectra of the low-field $\Delta m_S=1$ transitions for the phosphorescent triplet state of 2,2'-bipyridine in MeOH–H_2O (4 : 1 by volume). (a): With A-type excitation, (b): with B-type excitation.

various filter combinations: A-type excitation, Toshiba UV-D33S glass filter; B-type excitation, Toshiba UV-D33S and UV-31 glass filters to cut off the short-wavelength region and obtain a transmission of 40% at 310 nm. The results are shown in Fig. 8. The intensity of the ESR signal of the *s-cis* conformer relative to that of the *s-trans* conformer increases under lower-energy excitation (B-type excitation). Therefore, the *s-cis* conformer has an absorption at a longer wavelength region than the *s-trans* conformer. This is in accord with the fact that the absorption of BPY coordinated to Zn^{2+} is shifted to a longer wavelength region than that of

free *s-trans*-BPY.[7]

Two sets of ESR spectra corresponding to *s-cis*- and *s-trans*-BPY's were observed in mixtures of water with 2-propanol, ethylene glycol, 1,2-propanediol, 1,3-propanediol, or glycerol, as well as with methanol or 1-propanol. The triplet-state BPY, which has for many years been considered to be in the *s-trans* conformation in rigid solutions, can easily be trapped in the *s-cis* conformation by the interactions between BPY and the solvent molecules in mixtures of water with various alcohols.

On the other hand, only one set of ESR spectra corresponding to *s-trans*-BPY has been observed in ethanol and in ethanol–water mixtures. Ethanol is generally used as a matrix for isolating free radicals or excited molecules. It is particularly interesting that ethanol acts as an exceptional solvent on the conformation of BPY. The reason for the unexpected behavior of ethanol could not be found in the present work. However, it should be noted that two sets of triplet-state ESR spectra have been observed with steric interactions for 2,2′- and 3,3′-dimethylbiphenyls in neat ethanol solutions at 77K.[17]

The heat-capacity measurements by Suga and Seki suggest that a rapid cooling of liquid ethanol yields the glassy liquid, but a slow cooling of the liquid yields a crystalline phase.[18,19] The dependence of the sample-cooling rate on the stable conformation of BPY observed in *n*-PrOH–H_2O may be related to the structures of the rigid solutions. We would expect that the use of a semirigid molecule like BPY as a probe would contribute to a deeper understanding of the molecular aspect of the rigid solution.

The calculation of geometry optimization was carried out at The Computer Center of The Institute for Molecular Science, using the IMSPAK,[20] while that of the configuration interaction was done at The Computer Centre of The University of Tokyo, using the GSCF2.[21] The authors wish to thank Dr. Nobuhiro Kosugi, Department of Chemistry, The University of Tokyo, for his kind advice in the use of the GSCF2. The present work was partially supported by Grand-in Aid for Scientific Research No. 57470004 and No. 58740213 from the Ministry of Education, Science and Culture.

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