

The phosphorescent triplet states of aza-aromatics and their protonated cations in rigid solutions of ethanol and 1-butyl-3-methylimidazolium hexafluorophosphate

Ryuichiro Matsuo, Tomoaki Uchiyama, Kentarou Mogi, Shunya Kaneko, Kenta Kuwayama, Azusa Kikuchi, Mikio Yagi*

Department of Chemistry, Graduate School of Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

ARTICLE INFO

Article history:

Received 16 September 2008

Received in revised form 4 November 2008

Accepted 8 December 2008

Available online 24 December 2008

Keywords:

Triplet state

Electron paramagnetic resonance

Phosphorescence

Aza-aromatics

Ionic liquid

ABSTRACT

The lowest excited triplet (T_1) states of 2,2'-bipyridine (BPY), 6,6'-dimethyl-2,2'-bipyridine (DMBPY), 2,2'-biquinoline (BQ), 2-phenylpyridine (2-PPY), 3-phenylpyridine (3-PPY), 4-phenylpyridine (4-PPY), quinoline (QN) and isoquinoline (iso-QN) have been studied through measurements of the phosphorescence and EPR spectra in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) and in ethanol. BPY, DMBPY and BQ have the *trans* conformation in the ground (G) and T_1 states in [BMIM][PF₆] and in ethanol. Although only neutral forms of BPY, DMBPY, BQ and 4-PPY were observed in ethanol, their singly protonated cations were observed in [BMIM][PF₆] in the G and T_1 states. In the T_1 states, the solvent effects of [BMIM][PF₆] on the electron spin distributions of the aza-aromatics studied and their singly protonated cations are small.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

2,2'-Bipyridine (BPY) and 2,2'-biquinoline (BQ) are typical bidentate chelating agents for metal ions. The photophysics and photochemistry of complexes of BPY are under active investigation [1,2], with particular interest being taken in their application to solar-energy-conversion schemes [3]. The properties of BPY and BQ are closely related to their conformations. The *trans* and *cis* conformations are possible in BPY and BQ, as shown in Fig. 1. In solutions or in the crystalline states, the stable conformation of these metal-free ligands is *trans*, whereas in their metal complexes *cis* is preferred [4,5]. The Zn²⁺ complex with BPY has a very high quantum yield of fluorescence, while metal-free BPY has been considered to be nonfluorescent or very weakly fluorescent [6,7]. It is difficult to determine whether the observed change in the fluorescence property is due to the intrinsic effect of the coordination to Zn²⁺ ions or to the conformational change. The lack of data on the metal-free *cis* conformers of BPY and BQ leaves the question open, although theoretical calculations predict a rather small barrier for the *trans*–*cis* conformational change of BPY in the ground (G) state [8,9]. However, we have succeeded, by using a 2-propanol–water mixture as a host, in observing the luminescence and electron paramagnetic

resonance (EPR) spectra originating from the metal-free *cis* conformers of BPY, 6,6'-dimethyl-2,2'-bipyridine (DMBPY) and BQ at 77 K [6,10,11].

BPY and BQ are typical aromatic bases and the acid–base equilibria of the excited states of aza-aromatics have attracted considerable interest for many years [12–14]. The influence of protonation on the lowest excited triplet (T_1) states of aza-aromatic bases has been studied through EPR [15–20], optically detected magnetic resonance [21] and other optical techniques.

In the present work, we have determined the stable conformations of BPY, DMBPY and BQ in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]). We also have observed the singly protonated cations in the ionic liquid for BPY, DMBPY, BQ and 4-phenylpyridine (4-PPY) (Fig. 2), although only their neutral forms are observed in ethanol (EtOH). The effects of conformation and protonation on the zero-field splitting (ZFS) parameters of the T_1 states of the aza-aromatics are discussed.

2. Experimental

2.1. Materials

BPY, DMBPY, BQ, 2-phenylpyridine (2-PPY), 3-phenylpyridine (3-PPY), 4-PPY, quinoline (QN) and isoquinoline (iso-QN) were purchased from Tokyo Kasei Co. BPY and DMBPY were purified by sublimation in vacuo. BQ was purified by recrystallization from

* Corresponding author. Fax: +81 45 339 3948.

E-mail address: yagimiki@ynu.ac.jp (M. Yagi).

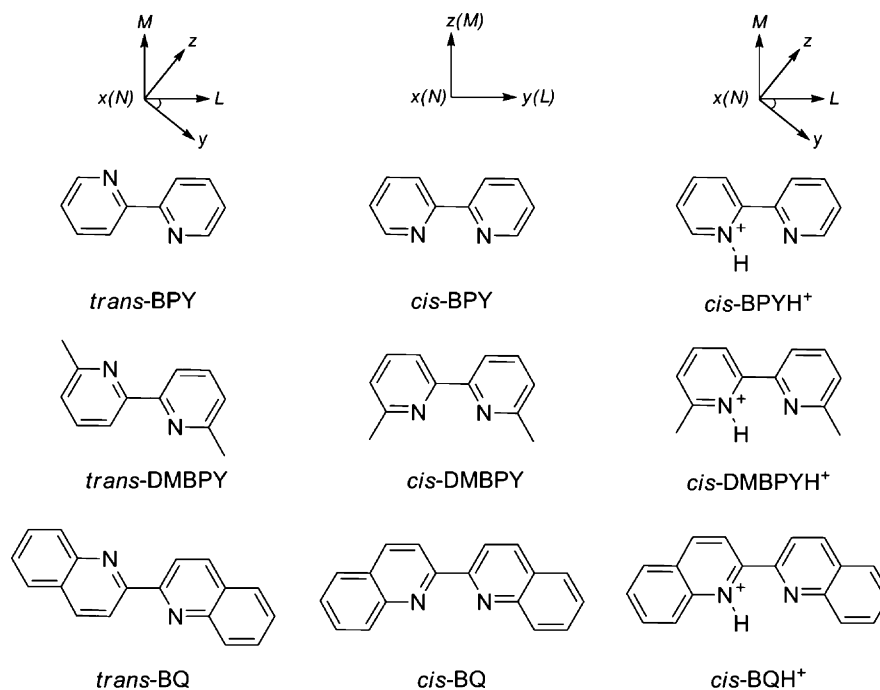


Fig. 1. Molecular structures and principal axes (x, y, z) of the ZFS tensors chosen for conformational isomers of BPY, DMBPY and BQ and for their singly protonated cations.

ethanol, followed by sublimation in vacuo. 2-PPY, 3-PPY and 4-PPY were purified by several recrystallization from water. QN and iso-QN were purified by the same method as reported in Ref. [22]. EtOH (Wako S. S. Grade) was used without further purification.

[BMIM][PF₆] was prepared by a standard procedure [23]. A colorless ionic liquid was obtained. We also prepared 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BDMIM][BF₄]) and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ([BDMIM][TFSI]) by the method described in the literature [24] in order to elucidate the source of the proton of the protonated species. The water content of the ionic liquids determined by the Karl–Fisher technique was about 90 ppm. [BMIM][PF₆] with a glass transition at $T_g = 196$ K forms a glass with a high cracking frequency at 77 K [25].

The concentrations of sample solutions were 1×10^{-4} mol dm⁻³ for BQ in EtOH–H₂SO₄ and 1×10^{-3} mol dm⁻³ for the other solutions.

2.2. Measurements

The UV absorption and fluorescence spectra were measured with a JASCO V-550 spectrophotometer and a JASCO FP-6500 spec-

trofluorometer, respectively. For the phosphorescence and EPR measurements, samples were excited with an Ushio 500 W Hg lamp equipped with an Asahi Technoglass UV-D33S glass filter, 5 cm of distilled water and a Copal DC-494 electromechanical shutter. For the phosphorescence measurements, the emissions from a sample were passed through a Jobin Yvon H-20UV spectrometer and detected by a Hamamatsu Photonics R453 photomultiplier tube.

The EPR spectra were measured at 77 K by a JEOL-JES-FE1XG spectrometer with 100 kHz magnetic field modulation at microwave frequencies close to 9.2 GHz. The static magnetic field was calibrated with an Echo Electronics EFM-2000AX proton NMR gauss meter.

3. Results

3.1. Optical properties

We took care to make [BMIM][PF₆] free from impurities because high pure ionic liquids are required for the optical and EPR measurements. The UV absorption spectrum of neat [BMIM][PF₆] at 25 °C is shown in Fig. 3d. The absorbance due to [BMIM][PF₆] in a 0.1-cm path length cuvette varies 0.099 at 250 nm, 0.024 at 300 nm,

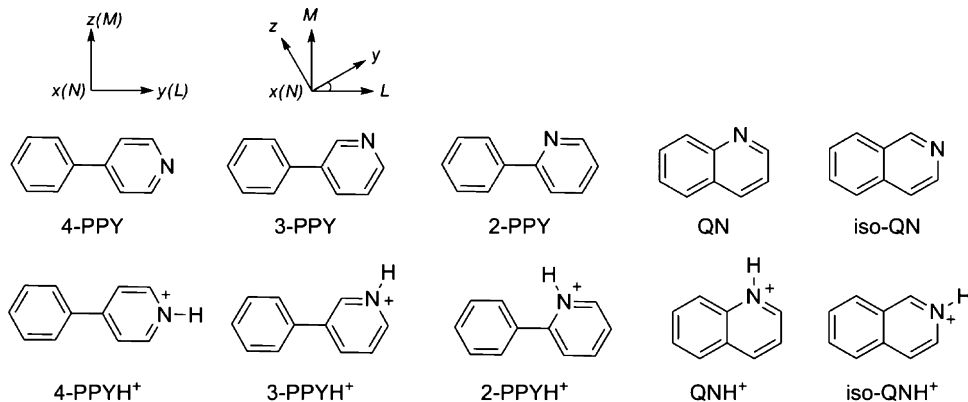


Fig. 2. Molecular structures and principal axes (x, y, z) of the ZFS tensors chosen for 2-PPY, 3-PPY, 4-PPY, QN and iso-QN and for their protonated cations.

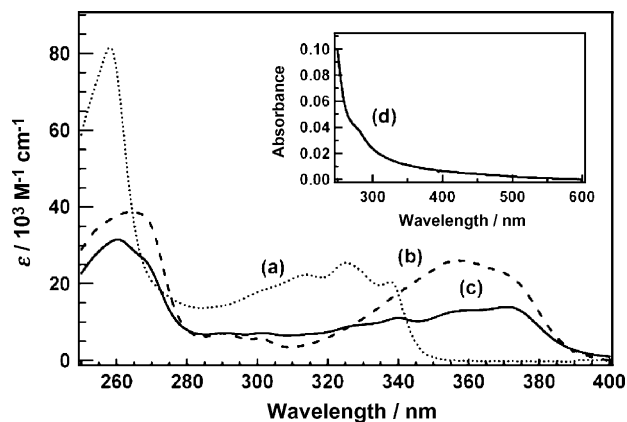


Fig. 3. UV absorption spectra of BQ and BQH⁺ (a) in EtOH (dotted line), (b) in H₂SO₄–EtOH (1.3 wt% of H₂SO₄) (broken line) and (c) in [BMIM][PF₆] (solid line) at 25 °C. (d) UV absorption spectrum of neat [BMIM][PF₆] (inset) at 25 °C.

0.0011 at 350 nm and 0.0007 at 400 nm, suggesting a good transparency in the ultraviolet and visible spectral region. On the other hand, Kato reported that no absorption signals were seen at wavelengths longer than 300 nm for pure [BMIM][PF₆] [26]. This shows that the absorption tail observed in the present work is caused by some impurities. However, all solvents were carefully checked for the absence of an extraneous fluorescence, phosphorescence and EPR signals before use under our experimental conditions. This is due to the fact that aza-aromatics studied are strongly luminescent and their T₁-state EPR signals are very strong in [BMIM][PF₆] at 77 K.

The UV absorption spectra of BPY, DMBPY, BQ, 2-PPY, 3-PPY, 4-PPY, QN and iso-QN were measured at 25 °C in EtOH–H₂SO₄ mixtures with various H₂SO₄ concentrations and in [BMIM][PF₆]. Fig. 3 shows the UV absorption spectra of BQ measured at 25 °C in EtOH, EtOH–H₂SO₄ and [BMIM][PF₆]. The observed spectrum (Fig. 3b) of BQ in EtOH–H₂SO₄ (1.3 wt% of H₂SO₄) was attributed to its singly protonated cation (BQH⁺). As is seen in Fig. 3c, the spectrum observed in [BMIM][PF₆] is attributed to the spectrum of the mixture of BQ and BQH⁺. This assignment is confirmed by EPR measurements as described below. In the same manner as for BQ, the coexistence of aza-aromatics with their singly protonated cations in [BMIM][PF₆] was observed for BPY, DMBPY and 4-PPY.

The emission spectra of BPY, DMBPY, BQ, 2-PPY, 3-PPY, 4-PPY, QN and iso-QN were measured in EtOH, EtOH–H₂SO₄ and [BMIM][PF₆] at 77 K. The emission spectra of DMBPY are shown in Fig. 4. The observed spectrum (Fig. 4b) of DMBPY in EtOH–H₂SO₄ (0.03 wt% of H₂SO₄) was attributed to its singly protonated cation (DMBPYH⁺). Fig. 4c shows the emission spectrum of DMBPY in [BMIM][PF₆] observed through the excitation at 320 nm where DMBPYH⁺ has an absorption maximum. As is clearly seen in Fig. 4c, the emission spectrum in [BMIM][PF₆] is attributed DMBPYH⁺, although the intensity ratio of fluorescence to phosphorescence for DMBPYH⁺ observed in [BMIM][PF₆] is larger than that observed in EtOH–H₂SO₄.

The phosphorescence spectra of BPY, DMBPY, BQ, 2-PPY, 3-PPY, 4-PPY, QN and iso-QN were measured in EtOH, EtOH–H₂SO₄ and [BMIM][PF₆] at 77 K. The phosphorescence spectra of 4-PPY are shown in Fig. 5. The observed spectrum (Fig. 5b) of 4-PPY in EtOH–H₂SO₄ (1.0 wt% of H₂SO₄) was attributed to its protonated cation (4-PPYH⁺). As is clearly seen in Fig. 5c, the phosphorescence spectrum observed in [BMIM][PF₆] is attributed to the spectrum of the mixture of 4-PPY and 4-PPYH⁺. This assignment is confirmed by EPR measurements as described below.

On protonation, the phosphorescence spectra of the aza-aromatics except 3-PPY are considerably red shifted. Applying the

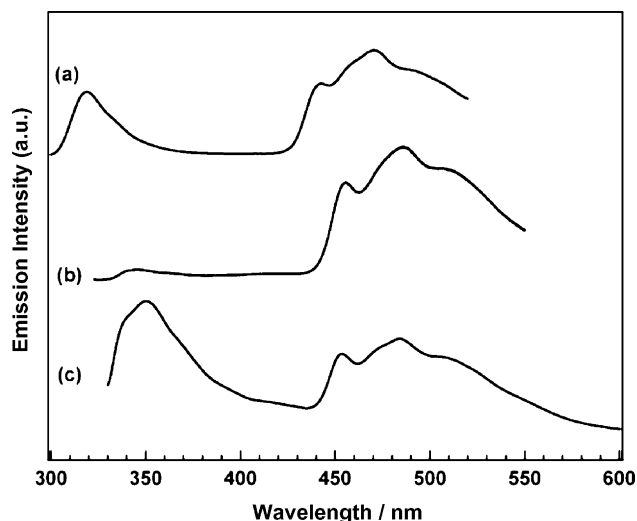


Fig. 4. Emission spectra of DMBPY (a) in EtOH, (b) in H₂SO₄–EtOH (0.03 wt% of H₂SO₄) and (c) in [BMIM][PF₆] at 77 K through the excitation (a) at 270 nm, (b) at 314 nm and (c) at 320 nm.

Förster cycle [12] to the phosphorescent states, the $\Delta pK_3(T_1)$ values were evaluated and are listed in Table 1. We can see from Table 1 that these aza-aromatics excited to the T₁ states become more basic than in the G states.

3.2. Zero-field splittings

The magnetic fine structure of the T₁ state in an external magnetic field **B** can be described by the following spin Hamiltonian:

$$\begin{aligned} H_S &= g\mu_B \mathbf{B} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \\ &= g\mu_B \mathbf{B} \cdot \mathbf{S} - X S_x^2 - Y S_y^2 - Z S_z^2 \\ &= g\mu_B \mathbf{B} \cdot \mathbf{S} + D[S_x^2 - (1/3)S^2] + E(S_y^2 - S_z^2) \end{aligned} \quad (1)$$

Here, $-X$, $-Y$, and $-Z$ are the principal values of the **D** tensor (ZFS tensor), and D and E are the ZFS parameters. The other symbols have their usual meaning. The anisotropy of the g tensor was disregarded. Assuming the molecular structure of the T₁ state to be planar in the rigid matrices at 77 K, the principal axes (x , y , z) of the ZFS tensors were taken to be as shown in Figs. 1 and 2. The ZFS parameters D and E are defined to be $D = -3X/2$ and $E = (Z - Y)/2$.

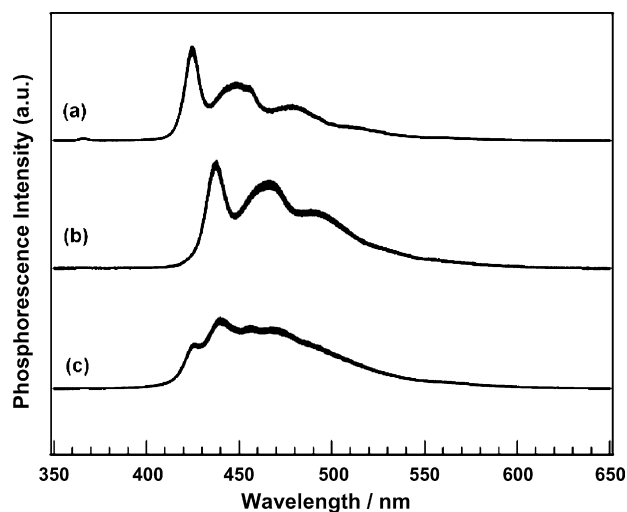


Fig. 5. Phosphorescence spectra of 4-PPY (a) in EtOH, (b) in H₂SO₄–EtOH (1.0 wt% of H₂SO₄) and (c) in [BMIM][PF₆] at 77 K.

Table 1
Zero-field splitting parameters (D and E), T_1 lifetimes (τ_T) and $\Delta pK_a(T_1)$ values observed at 77 K.

| Molecule | Host | D (cm ⁻¹) | E (cm ⁻¹) | τ_T (s) ^c | $\Delta pK_a(T_1)$ ^d |
|---------------------------------|--|-------------------------|-------------------------|---------------------------|---------------------------------|
| <i>trans</i> -BPY | EtOH | 0.1093 | -0.0126 | 0.96 | - |
| <i>trans</i> -BPY | [BMIM][PF ₆] | 0.1093 | -0.0126 | 0.96 | - |
| <i>cis</i> -BPY ^a | <i>i</i> -PrOH-H ₂ O ^b | 0.1101 | -0.0051 | 0.95 | - |
| <i>cis</i> -BPYH ⁺ | H ₂ SO ₄ -EtOH | 0.1038 | -0.0093 | 1.23 | 0.9 |
| <i>cis</i> -BPYH ⁺ | [BMIM][PF ₆] | 0.1043 | -0.0091 | 0.98 | 0.7 |
| <i>trans</i> -DMBPY | EtOH | 0.1052 | -0.0170 | 0.85 | - |
| <i>trans</i> -DMBPY | [BMIM][PF ₆] | 0.1037 | -0.0173 | 0.84 | - |
| <i>cis</i> -DMBPY ^a | <i>i</i> -PrOH-H ₂ O ^b | 0.1038 | -0.0054 | 0.78 | - |
| <i>cis</i> -DMBPYH ⁺ | H ₂ SO ₄ -EtOH | 0.0971 | -0.0108 | 0.89 | 1.3 |
| <i>cis</i> -DMBPYH ⁺ | [BMIM][PF ₆] | 0.0985 | -0.0108 | 0.77 | 1.2 |
| <i>trans</i> -BQ | EtOH | 0.0989 | -0.0365 | 0.80 | - |
| <i>trans</i> -BQ | [BMIM][PF ₆] | 0.0974 | -0.0364 | 0.86 | - |
| <i>cis</i> -BQ ^a | <i>i</i> -PrOH-H ₂ O ^b | 0.0915 | -0.0209 | 0.68 | - |
| <i>cis</i> -BQH ⁺ | H ₂ SO ₄ -EtOH | 0.0823 | -0.0188 | 0.20 | 2.8 |
| <i>cis</i> -BQH ⁺ | [BMIM][PF ₆] | 0.0830 | -0.0186 | 0.14 | 2.9 |
| 2-PPY | EtOH | 0.1098 | -0.0064 | 2.2 | - |
| 2-PPY | [BMIM][PF ₆] | 0.1097 | -0.0066 | 2.1 | - |
| 2-PPYH ⁺ | H ₂ SO ₄ -EtOH | 0.1029 | -0.0087 | 3.5 | 0.7 |
| 3-PPY | EtOH | 0.1085 | -0.0041 | 3.0 | - |
| 3-PPY | [BMIM][PF ₆] | 0.1088 | -0.0041 | 2.7 | - |
| 3-PPYH ⁺ | H ₂ SO ₄ -EtOH | 0.1025 | -0.0083 | 3.9 | 0.1 |
| 4-PPY | EtOH | 0.1125 | -0.0047 | 2.6 | - |
| 4-PPY | [BMIM][PF ₆] | 0.1124 | -0.0045 | 2.0 | - |
| 4-PPYH ⁺ | H ₂ SO ₄ -EtOH | 0.1038 | -0.0094 | 5.5 | 1.4 |
| 4-PPYH ⁺ | [BMIM][PF ₆] | 0.1049 | -0.0092 | 5.0 | 1.6 |
| QN | EtOH | 0.1010 | -0.0163 | 1.3 | - |
| QN | [BMIM][PF ₆] | 0.1014 | -0.0165 | 1.2 | - |
| QNH ⁺ | H ₂ SO ₄ -EtOH | 0.0922 | -0.0148 | 1.8 | 0.9 |
| iso-QN | EtOH | 0.0999 | -0.0113 | 0.88 | - |
| iso-QN | [BMIM][PF ₆] | 0.1001 | -0.0116 | 0.79 | - |
| iso-QNH ⁺ | H ₂ SO ₄ -EtOH | 0.0928 | -0.0111 | 1.0 | 0.6 |

^a Ref. [6].

^b Observed in *i*-PrOH-H₂O (33 wt% of *i*-PrOH).

^c Obtained from the decay of the EPR signal.

^d $\Delta pK_a(T_1) = pK_a(T_1) - pK_a(G)$.

The EPR spectra of the T_1 states of BPY, DMBPY, BQ, 2-PPY, 3-PPY, 4-PPY, QN and iso-QN were measured in EtOH, EtOH-H₂SO₄ and [BMIM][PF₆] at 77 K. The EPR spectra of the $\Delta M_S = \pm 2$ transitions for the T_1 state of BQ are shown in Fig. 6. As is clearly seen in Fig. 6c, the EPR spectrum observed in [BMIM][PF₆] is attributed to the spectrum of the mixture of BQ and BQH⁺. The EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 states of BPY and 4-PPY are shown in Fig. 7. The assignments of the observed EPR signals of BPY, BQ, 4-PPY and their singly protonated cations have already been carried out with the aid of a stretched-polymer-film technique [8,27,28]. The observed ZFS parameters and lifetimes in the T_1 states obtained from the decay curves of the EPR signals are listed in Table 1.

4. Discussion

4.1. Conformers and nature of the T_1 states

The *cis* and *trans* conformations are possible in BPY, DMBPY and BQ. We developed the stretched-polymer-film technique for determining the *cis* and *trans* conformations of the T_1 states of these molecules [29]. The ZFS parameters of the conformational isomers of these molecules have been obtained using a 2-propanol-water mixture as a host [6]. These values are given in Table 1. We can see from Table 1 that the ZFS values of BPY, DMBPY and BQ obtained in [BMIM][PF₆] are almost the same as those of the *trans* isomers. The conformations of BPY, DMBPY and BQ in [BMIM][PF₆] can reasonably be assigned to the *trans* conformers in the T_1 states at 77 K.

As is clearly seen in Table 1, the D values obtained are about 0.1 cm⁻¹ and the lifetimes of the T_1 states are 0.14–5.5 s. Therefore, the T_1 states possess an almost pure $^3\pi\pi^*$ character in all

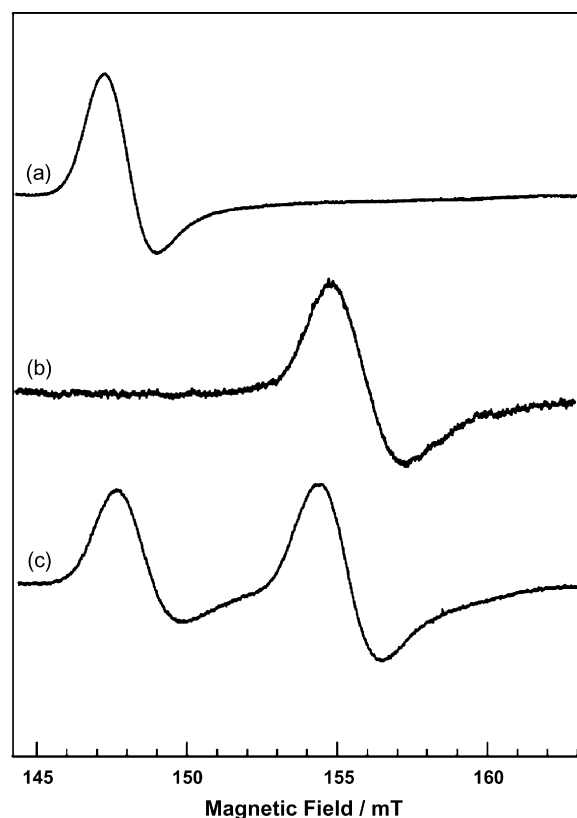


Fig. 6. EPR spectra of the $\Delta M_S = \pm 2$ transitions for the T_1 state of BQ (a) in EtOH, (b) in H₂SO₄-EtOH (1.3 wt% of H₂SO₄) and (c) in [BMIM][PF₆] at 77 K.

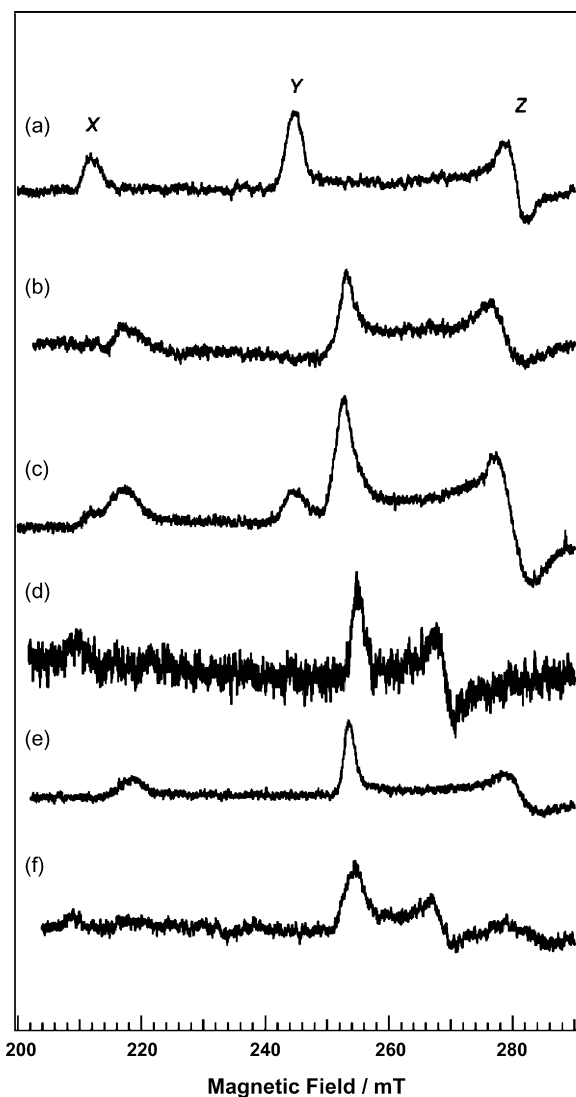


Fig. 7. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 states of BPY (a) in EtOH, (b) in H_2SO_4 –EtOH (0.03 wt% of H_2SO_4) and (c) in [BMIM][PF₆] and of 4-PPY (d) in EtOH, (e) in H_2SO_4 –EtOH (1.0 wt% of H_2SO_4) and (f) in [BMIM][PF₆] at 77 K.

cases in EtOH and in [BMIM][PF₆]. The ZFS parameters observed in [BMIM][PF₆] are almost the same as those observed in EtOH. The solvent effects of [BMIM][PF₆] on the electron spin distributions of the T_1 states are small in all cases.

Fig. 4b and c show the emission spectra of DMBPYH⁺ in EtOH and in [BMIM][PF₆], respectively. The observed effect of the ionic liquid on the intensity ratio of fluorescence to phosphorescence for DMBPYH⁺ may be explained by an increment of the $^1\pi\pi^*$ character in the S_1 state because the T_1 state of DMBPYH⁺ possesses an almost pure $^3\pi\pi^*$ character in both EtOH and [BMIM][PF₆]. The fluorescence of DMBPYH⁺ is expected to be enhanced, considering that the $S_1 \rightarrow T_1$ intersystem crossing between $^1\pi\pi^*$ and $^3\pi\pi^*$ states should be much slower than that between $^1n\pi^*$ and $^3\pi\pi^*$ states, as suggested by El-Sayed [30].

4.2. Effects of conformation and protonation on the zero-field splittings

In order to elucidate the effects of the conformation and protonation on the zero-field splittings, the ZFS parameters of *trans*-BPY, *cis*-BPY and *cis*-BPYH⁺ were calculated using semiempirical molecular orbitals. The details of the procedure are the same as those

Table 2

Calculated zero-field splitting parameters for the T_1 states of *trans*-BPY, *cis*-BPY and *cis*-BPYH⁺.

| Molecule | X (cm ⁻¹) | Y (cm ⁻¹) | Z (cm ⁻¹) | D (cm ⁻¹) ^a | E (cm ⁻¹) ^b |
|-------------------------------|-----------------------|-----------------------|-----------------------|------------------------------------|------------------------------------|
| <i>trans</i> -BPY | -0.0806 | 0.0730 | 0.0076 | 0.1209 | -0.0327 |
| <i>cis</i> -BPY | -0.0820 | 0.0409 | 0.0410 | 0.1229 | 0.0001 |
| <i>cis</i> -BPYH ⁺ | -0.0580 | 0.0367 | 0.0213 | 0.0870 | -0.0077 |

^a $D = -3X/2$.

^b $E = (Z - Y)/2$.

described in the previous papers [18,19]. The parameter appearing in the Coulomb integral, $\alpha_N^+ = \alpha + h_N^+ \beta$, was chosen to be $h_N^+ = 2$ for the singly protonated cations [31]. The electron spin dipole–dipole interactions were calculated by assuming the hypothetical structures with which the length of the C–C bond between the two pyridine rings was taken to be 150 pm and the C–C and C–N bonds in the pyridine rings were taken to be 139 pm [4]. The molecules were assumed to be planar in the T_1 states. The wavefunctions used were obtained from the Pariser–Parr–Pople-type calculations by including configurations arising from all the single excitations relative to the G state. Once the open shell orbital wavefunction of the T_1 state $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ is specified, the ZFS parameters D and E are calculated from the following equations:

$$D = \frac{\mu_0}{4\pi} \left(\frac{3}{4}\right) (g\mu_B)^2 \int \Phi(\mathbf{r}_1, \mathbf{r}_2) \frac{r_{12}^2 - 3x_{12}^2}{r_{12}^5} \Phi(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2 \quad (2)$$

$$E = \frac{\mu_0}{4\pi} \left(\frac{3}{4}\right) (g\mu_B)^2 \int \Phi(\mathbf{r}_1, \mathbf{r}_2) \frac{z_{12}^2 - y_{12}^2}{r_{12}^5} \Phi(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2 \quad (3)$$

The calculated ZFS parameters are given in Table 2. We can see from this table that the calculated ZFS values are sufficiently consistent with the observed ones. Assuming that the *cis* isomer of BPY has C_{2v} symmetry in the T_1 state, the non-zero off-diagonal elements of the ZFS tensor appear for the *trans* isomer while all off-diagonal elements are zero for the *cis* isomer. As a result, the *trans* isomer is expected to possess a larger $|E|$ value than the *cis* isomer as is observed.

As is clearly seen in Table 1, following the singly protonation of the aza-aromatics studied, the $|D|$ values decrease. This result suggests that some expansion of the electron spin distribution occurs on protonation. In that case the π electron structure changes significantly in the vicinity of the nitrogen atom. In the T_1 state of biphenyl, the spin densities ρ_i at the *ortho*-, *meta*- and *para*-carbon atoms are $\rho_{para} > \rho_{ortho} > \rho_{meta}$ [32]. On protonation, therefore, the changes in $|D|$, $|\Delta D|$, are predicted to be $|\Delta D_{4-PPY}| > |\Delta D_{2-PPY}| > |\Delta D_{3-PPY}|$ for the T_1 states of aza-biphenyls, as are observed. In the T_1 states of naphthalene and aza-naphthalenes, the spin densities at the α -position are high compared with those at the β -position [33]. On protonation, the change in $|D|$ for QN is expected to be larger than that for iso-QN, as is observed. It should be noted that the phosphorescence measurements give $\Delta pK_a(T_1)_{4-PPY} > \Delta pK_a(T_1)_{2-PPY} > \Delta pK_a(T_1)_{3-PPY}$ and $\Delta pK_a(T_1)_{QN} > \Delta pK_a(T_1)_{iso-QN}$, in agreement with the changes in $|D|$.

In the present work, the singly protonated cations of BPY, DMBPY, BQ and 4-PPY were observed in [BMIM][PF₆], while only neutral forms of 2-PPY, 3-PPY, QN and iso-QN were observed. This may be due to the facts that the singly protonated cations of *cis*-BPY, *cis*-DMBPY and *cis*-BQ are considerably stabilized by the [N–H⁺...N] interaction [5,34,35] and 4-PPY is the most basic among phenylpyridines [36]. However, the reason for the lack of the protonated cations of QN and iso-QN is unknown.

The problem we are faced with is the source of the proton of the protonated species in [BMIM][PF₆]. The presence of water in [BMIM][PF₆] cannot be neglected. One possible explanation of the source of the proton arises from the presence of HF as a hydrolytic

decomposition of $[\text{PF}_6]^-$ anion [37], although the addition of water to $[\text{BMIM}][\text{PF}_6]$ up to 7500 ppm does not affect the relative concentration of the singly protonated species.

Another possible explanation may arise from the presence of the most acidic H atom of the imidazolium ring C2 [38]. The UV absorption spectra of DMBPY were measured at room temperature in $[\text{BDMIM}][\text{BF}_4]$ and in $[\text{BDMIM}][\text{TFSI}]$ where the H atom of the imidazolium ring C2 was replaced by the methyl group. However, the observed UV absorption spectra are attributed to the spectra of the mixture of DMBPY and DMBPYH⁺.

5. Conclusions

Our optical and EPR experiments indicate that the stable conformation of BPY, DMBPY and BQ is *trans* in the G and T₁ states in both EtOH and $[\text{BMIM}][\text{PF}_6]$. Singly protonated cations of BPY, DMBPY, BQ and 4-PPY were observed in $[\text{BMIM}][\text{PF}_6]$, while only their neutral forms were observed in EtOH without sulfuric acid. The solvent effects of $[\text{BMIM}][\text{PF}_6]$ on the electron spin distributions in the T₁ states of the aza-aromatics studied and their singly protonated cations are small.

Acknowledgements

The authors wish to thank Professor Masayoshi Watanabe, Dr. Hiroyuki Tokuda and Mr. Kazuhide Ueno of Yokohama National University for their helpful advice concerning the synthesis of $[\text{BMIM}][\text{PF}_6]$ and the Karl–Fisher titration. They also wish to thank Ms. Michiko Matsumoto, Mr. Ryuichi Sawagashira and Mr. Daisuke Nakajima of our laboratory for their help. This work was supported in part by Grants-in-Aid for Scientific Research No. 15550009 and in Priority Areas “New Frontiers in Photochromism (No. 471)” from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

- [1] C. Kaes, A. Katz, M.W. Hosseini, Chem. Rev. 100 (2000) 3553–3590.

- [2] C. Lapouge, G. Buntinx, O. Poizat, Chem. Phys. 348 (2008) 209–214.
 [3] M.S. Wrighton, J. Chem. Ed. 60 (1983) 877–881.
 [4] L.L. Merritt Jr., E.D. Schroeder, Acta Cryst. 9 (1956) 801–804.
 [5] N. Nakamoto, J. Phys. Chem. 64 (1960) 1420–1425.
 [6] M. Yagi, T. Kaneshima, Y. Wada, K. Takemura, Y. Yokoyama, J. Photochem. Photobiol. A: Chem. 84 (1994) 27–32.
 [7] J. Kotlicka, Z.R. Grabowski, J. Photochem. 11 (1979) 413–418.
 [8] M. Yagi, K. Makiguchi, A. Ohnuki, K. Suzuki, J. Higuchi, S. Nagase, Bull. Chem. Soc. Jpn. 58 (1985) 252–257.
 [9] A.H. Göller, U.-W. Grummt, Chem. Phys. Lett. 354 (2002) 233–242.
 [10] M. Yagi, H. Shirai, J. Ohta, J. Higuchi, Chem. Phys. Lett. 160 (1989) 13–16.
 [11] M. Yagi, B.D. Schlyer, A.H. Maki, Chem. Phys. 157 (1991) 209–216.
 [12] Z.R. Grabowski, A. Grabowska, Z. Physik. Chem. NF 101 (1976) 197–208.
 [13] M. Yagi, Y. Deguchi, Y. Shioya, J. Higuchi, Chem. Phys. Lett. 144 (1988) 412–416.
 [14] M. Yagi, S. Yamaguchi, M. Noda, K. Seki, Appl. Magn. Reson. 18 (2000) 385–395.
 [15] A. Chodkowska, Z.R. Grabowski, Chem. Phys. Lett. 24 (1974) 11–14.
 [16] H. Bulska, A. Chodkowska, A. Grabowska, B. Pakula, Z. Slanina, J. Lumin. 10 (1975) 39–57.
 [17] M. Yagi, I. Itoh, A. Komura, K. Hayashi, J. Higuchi, Chem. Phys. Lett. 211 (1993) 179–182.
 [18] M. Noda, K. Matsushima, K. Seki, M. Yagi, Chem. Phys. Lett. 296 (1998) 599–604.
 [19] M. Deguchi, D. Suzuki, R. Ito, M. Matsumoto, M. Yagi, Spectrochim. Acta A 61 (2005) 1147–1151.
 [20] R. Ito, D. Suzuki, Y. Yokoyama, M. Yagi, Chem. Phys. Lett. 420 (2006) 261–266.
 [21] A.G. Motten, A.L. Kwiram, J. Chem. Phys. 75 (1981) 2608–2615.
 [22] A. Komura, K. Uchida, M. Yagi, J. Higuchi, J. Photochem. Photobiol. A: Chem. 42 (1988) 293–300.
 [23] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, Chem. Commun. (1998) 1765–1766.
 [24] V. Farmer, T. Welton, Green Chem. 4 (2002) 97–102.
 [25] W. Xu, E.I. Cooper, C.A. Angell, J. Phys. Chem. B 107 (2003) 6170–6178.
 [26] R. Kato, Chem. Lett. 36 (2007) 1256–1257.
 [27] M. Yagi, A. Saitoh, K. Takano, K. Suzuki, J. Higuchi, Chem. Phys. Lett. 118 (1985) 275–278.
 [28] M. Yagi, M. Matsunaga, J. Higuchi, Chem. Phys. Lett. 86 (1982) 219–222.
 [29] J. Higuchi, M. Yagi, T. Iwaki, M. Bunden, K. Tanigaki, T. Ito, Bull. Chem. Soc. Jpn. 53 (1980) 890–895.
 [30] M.A. El-Sayed, Annu. Rev. Phys. Chem. 26 (1975) 235–258.
 [31] A. Streitwieser Jr., Molecular Orbital Theory for Organic Chemists, John Wiley & Sons, New York, 1961, p. 135.
 [32] C.A. Hutchison Jr., M.D. Kemple, J. Chem. Phys. 74 (1981) 192–199.
 [33] M. Yagi, K.S. Uchida, J. Higuchi, J. Magn. Reson. 71 (1987) 303–312.
 [34] S.T. Howard, J. Am. Chem. Soc. 118 (1996) 10269–10274.
 [35] U.-W. Grummt, S. Erhardt, J. Mol. Struct. (THEOCHEM) 685 (2004) 133–137.
 [36] J. Kubin, A.C. Testa, J. Photochem. Photobiol. A: Chem. 83 (1994) 91–96.
 [37] R.P. Swatloski, J.D. Holbrey, R.D. Rogers, Green Chem. 5 (2003) 361–363.
 [38] S.I. Nikitenko, C. Hennig, M.S. Grigoriev, C.L. Naour, C. Cannes, D. Trubert, E. Bossé, C. Berthon, P. Moisy, Polyhedron 26 (2007) 3136–3142.