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Magnetic Circular Dichroism Studies of Bipyridyls

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The magnetic circular dichroism (MCD) and UV absorption spectra of 2,2′- and 4,4′-bipyridyl in cyclohexane and sulfuric acid were measured at room temperature. The MCD spectrum of 2,2′-bipyridyl is different from that of 4,4′-bipyridyl, reflecting the difference in molecular symmetry between them. The absorption and MCD spectral profiles of 2,2′-bipyridyl in cyclohexane are different from those of 2,2′-bipyridyl in mineral acids, in this system protonation taking place on the nitrogen atoms to give a mono- or di-cation with low symmetry. On the contrary, the MCD spectra of 4,4′-bipyridyl in cyclohexane and in acidic media at pH 0.98 exhibit a similar spectral profile to each other due to the D_2 symmetry being retained in 4,4′-bipyridyl. Theoretical calculations were carried out on the basis of the PPP-SCF-CI method to get a reasonable explanation for the observed MCD spectra. The assignments of the MCD bands of these compounds are given and their dihedral angles are estimated.

According to Fisher-Hjalmars' consideration,[1] the repulsion among ortho-protons in biphenyl plays an important role in determining its stable conformation. The twisted angle around the central bond (see Fig. 1) is given on a balance between two effects, the conjugation between the two benzene rings and the repulsion among the nonbonded atoms, especially among the ortho-protons. Accordingly, on substitution with bulky groups at the ortho-positions the dihedral angle of biphenyl will increase due to an appreciable increase in the steric repulsion, giving rise to a hypsochromic effect on the transition energy and a hypochromic effect on the intensity of the conjugation band.[2]

It has been known from an X-ray diffraction study that 2,2′-bipyridyl has a trans-planar structure.[3] The molecular structure in solvents where the protonation of the bipyridyl moiety is prevented is expected to be planar because of the absence of the repulsion among the protonated protons. On the other hand, in 4,4′-bipyridyl there exists a repulsion among the ortho-protons as in biphenyl. Accordingly, the two pyridine rings of 4,4′-bipyridyl in solution are expected to be twisted around the central bond.

For bipyridyls, abbreviated to B hereafter, the equilibria are expected to be established in acidic media,

$$BH_2^{2+} \overset{K_2}{\rightleftharpoons} BH^+ + H^+ \overset{K_1}{\rightleftharpoons} B + 2H^+,$$

where K_1 and K_2 are the acid dissociation constants. There exist three species, a neutral species B and protonated species BH^+ and BH_2^{2+}, in acidic solutions. Nakamoto[4] investigated the equilibrium between the neutral molecule B and the mono-cation BH^+ of 2,2′-bipyridyl by observing UV absorption spectra at various pH values. According to this investigation 2,2′-bipyridyl exists mainly in a mono-cationic form at $pH \simeq 1.80$ and in a neutral form at $pH > 9.15$. Krumholz[5] determined pK_1 of 2,2′-bipyridyl to be 4.44 based on the potentiometric titration method. This value is in good agreement with that obtained by Nakamoto.[4]

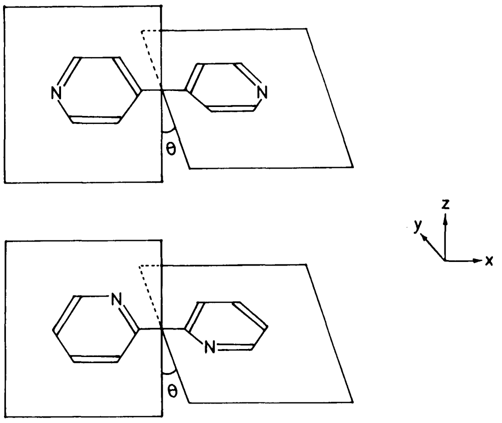

Fig. 1. Molecular skeletons and choice of axis for 4,4′-(top) and 2,2′-bipyridyl (bottom).

On the other hand, pK_1 and pK_2 for 4,4′-bipyridyl were evaluated to be 4.82 and 3.17, respectively.[5] Therefore, 4,4′-bipyridyl exists mainly as a di-cation at $pH < 2.0$.

In 2,2′-bipyridyldium, two pyridinium rings seem to be twisted around the central bond due to the repulsion among the ortho-protons. However, Nakamoto[4] has suggested that the planar trans-configuration is preferable for 2,2′-bipyridyldium in view of the charge distribution. Borgen *et al.*[6] have drawn the same conclusion for the di-cation of 2,2′-bipyridyl on the basis of a CNDO calculation.

The 2,2′-bipyridylium cation was confirmed to have a cis-form by Nakamoto[4] based on a comparative absorption spectroscopic study between the mono-cation and the metal-chelate compound $[Ni(bypy)_3]Cl_2$ in which bipyridyl is forced to take a cis-form. In the mono-cation the two pyridine rings seem to be twisted to some extent around the central bond due to the repulsion among the ortho-protons.

In this work 2,2′- and 4,4′-bipyridyl in cyclohexane and acids were reexamined from the view point of MCD spectroscopy. A quantum mechanical calculation based on the PPP method was carried out to get a reasonable characterization and assignment of observed MCD bands. A comparison between experimental and theoretical results has led to an estimation of the dihedral angles of bipyridyls in solution.

Experimental

Commercially available 2,2′- and 4,4′-bipyridyl were purified by sublimation under reduced pressure. The cyclohexane and sulfuric acid were of spectro-grade and used as solvents without further purification. The buffer solutions were $CH_3COOH+CH_3COOK$ with pH=3.0—6.0 and $NaOH+KH_2PO_4$ with pH=6.97.

MCD and UV spectra were measured with a JASCO-J500C recordig circular dichrometer equipped with a 1.14 T electromagnet and with a JASCO-UVIDEC-J510 recording spectrophotometer, respectively. All measurements were carried out at room temperature.

Theoretical

The electronic transition energies, oscillator strenghths, and Faraday *B* values of the bipyridyls and their cations were evaluatd by the use of the PPP method[7] together with configuration interaction among singly excited configurations with transition energies below 10 eV. One-center core and repulsion integrals were evaluated from valence state ionization potentials and electron affinities. Two-center core integrals, β_{pq}, were calculated by use of the Wolfsberg-Helmholz equation,[8] except β_{CN^+} for which the value of —2.74 eV was used.[9] Two-center repulsion integrals were evaluated by use of the Nishimoto-Mataga equation.[10] The repulsion integrals, γ_{pq}, within the pyridine ring, were evaluated according to the usual formula

$$\gamma_{pq} = \frac{14.397}{R_{pq} + a_{pq}}, \tag{1}$$

with

$$a_{pq} = \frac{28.794}{\gamma_{pp} + \gamma_{qq}}, \tag{2}$$

where R_{pq} is the distance between atoms p and q, and γ_{pp} stands for the one-center repulsion integral. The repulsion integral, γ_{pq}, in which atoms p and q belong to different pyridine rings was calculated using Eq. 1 with the following modification on a_{pq}:

$$a_{pq} = \frac{28.794}{(\gamma_{pp}+\gamma_{qq})\cos^2\theta+(\gamma'_{pp}+\gamma'_{qq})\sin^2\theta}, \tag{3}$$

$$\gamma'_{pp} = \gamma_{pp} - 6F_2, \tag{4}$$

where θ is the dihedral angle and F_2 is the Slater-Condon parameter. The bond distances and bond angles of 2,2′-bipyridyl were taken from X-ray diffraction data.[3] The molecular geometry for the pyridine ring in 4,4′-bipyridyl was taken from electron diffraction data for pyridine.[11] The molecular structure of the cation was assumed to be identical with that of the corresponding neutral molecule. The coordinate system is shown in Fig. 1. The x axis lies along the long molecular axis and the y axis bisects the dihedral angle, θ.

The theoretical Faraday *B* term associated with an electronic transition, $j \leftarrow a$, is expressed as[12]

$$\begin{aligned} B(j\leftarrow a) = \mathrm{Im}[&\sum_{k\neq a}\{\langle k|\vec{\mu}|a\rangle/(E_k-E_a)\} \times \\ &\langle a|\vec{m}|j\rangle \times \langle j|\vec{m}|k\rangle \\ &+\sum_{k\neq j}\{\langle j|\vec{\mu}|k\rangle/(E_k-E_j)\} \times \\ &\langle a|\vec{m}|j\rangle \times \langle k|\vec{m}|a\rangle], \end{aligned} \tag{5}$$

where $\vec{\mu}$ and $\vec{m}$ denote the magnetic and electric moment operators, respectively. The quantities in the denominator, *e.g.*, E_k, is the energy of the *k*th state. The transition dipole moments were estimated by the dipole length method using the Slater AO's. The atomic integrals of the electric and magnetic dipole moments were retained only for the nearest neighbor atoms, and were neglected for the distant atoms because they are too small to give any decisive effect on calculated results. The deorthogonalized set of atomic orbitals obtained by the inverse Löwdin procedure[13] was used for the calculation of these quantities. The calculation was carried out using an ACOS-700 computer at The Computer Center of Tohoku University.

Results and Discussion

2,2′-Bipyridyl and Its Cations. The UV absorption spectrum of 2,2′-bipyridyl in cyclohexane is illustrated in Fig. 2 (left), showing absorption maxima at 35400, 40800, and 42000 cm^{-1}. The MCD spectrum exhibits a negative peak at 36000 cm^{-1} and a positive extreme at 42300 cm^{-1}. Another MCD band appears in the wave number region higher than 47000 cm^{-1}. From a comparison of the 2nd MCD band with the corresponding absorption band, the fine structure of the latter is considered to be vibrational in origin. In fact, the UV absorption spectrum of 2,2′-bipyridyl in basic media shows a structureless single peak in the same region.

The calculated Faraday *B* values and oscillator strengths of 2,2′-bipyridyl are schematically represented in Fig. 2 (right). For convenience $-B$ is taken on the ordinate since the Faraday parameter *B* appears as $-B$ in the expression of the molar ellipticity, $[\theta]_M$. It is assumed in the present calculation that 2,2′-bipyridyl has the trans-planar structure ($\theta=0°$). The 1st and 2nd MCD bands of 2,2′-bipyridyl are assigned to the 1st and 2nd $^1B_u \leftarrow {}^1A_g$ electronic transitions, respectively. The strong negative MCD band in the energy region higher than 47000 cm^{-1} is assigned to the predicted $^1B_u \leftarrow {}^1A_g$ (51100 cm^{-1}) transition.

The UV absorption spectra of 2,2′-bipyridyl in sulfuric acid of various concentrations between 0.102 and 3.87 M (1 M=1 mol dm^{-3}) are illustrated in Fig. 3, where three isosbestic points are observed, exhibiting the equilibrium $BH_2^{2+} \rightleftarrows BH^+ + H^+$. 2,2′-Bipyridyl in sulfuric acid of 0.102 M exists in a mono-cationic form, exhibiting the absorptions at 33300 and 41700 cm^{-1} (the dotted line in Fig. 3). Increasing the concentration of the acid causes the equilibrium to shift toward left so as to give the absorption at 35000 cm^{-1} characteristic of the di-cation (the solid line). No further change in spectral profile takes place at concentrations lower (higher) than 0.102 M (3.87 M). It is clear from these facts that 2,2′-bipyridyl in sulfuric acid with concentrations higher than 3.87 M exists as the di-cation, and that 2,2′-bipyridyl in sulfuric acid with pH's lower than 1.80 exists as the mono-cation.

The absorption spectrum of 2,2′-bipyridyl in sulfuric acid at pH 1.22 is included in Fig. 4, which reveals absorptions at 33300 and 41700 cm^{-1}, characteristic of the mono-cationic species. The intensity of the former

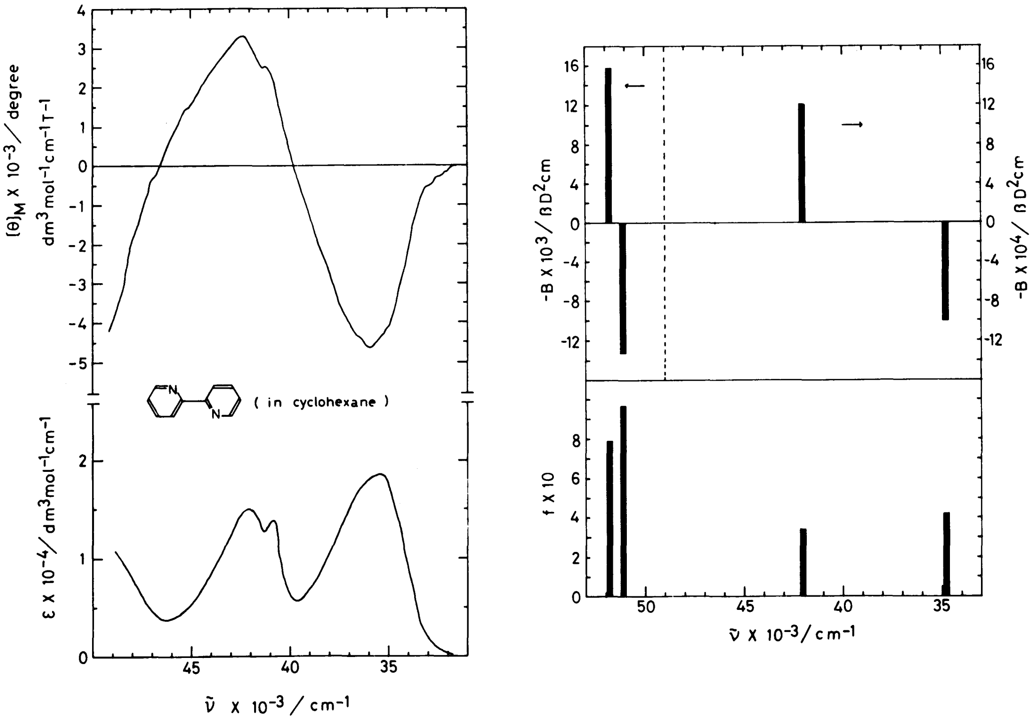

Fig. 2. The observed MCD (left top) and absorption (left bottom) spectra of 2,2′-bipyridyl in cyclohexane at room temperature. Theoretical *B* values (right top) and oscillator strengths (right bottom) calculated for a trans structure with θ=0°.

Table 1. Theoretical transition energies ($\tilde{\nu}$), oscillator strengths (f), and B values (B) of 2,2′-bipyridyl

Compound	Symmetry	$\tilde{\nu}\times10^{-3}$ cm^{-1}	f	$-B\times10^5$ βD^{2}cm	$\tilde{\nu}\times10^{-3}$ cm^{-1}	$[\theta]_M^{max}\times10^{-3}$
2,2′-Bipyridyl	$^1B_u \leftarrow {}^1A_g$	34.8	0.42	−100.9	35.97	−4.64
(θ=0°)	$^1A_g \leftarrow {}^1A_g$	37.5	forb.	0.0	—	—
	$^1B_u \leftarrow {}^1A_g$	42.1	0.34	120.4	42.28	−3.28
	$^1A_g \leftarrow {}^1A_g$	47.4	forb.	0.0	—	—
	$^1A_g \leftarrow {}^1A_g$	49.4	forb.	0.0	—	—
	$^1B_u \leftarrow {}^1A_g$	51.1	0.97	1335.3	—	—
2,2′-Bipyridyl		28.4	0.47	−6.1	33.70	−2.19
mono-cation		33.5	0.11	−96.0	—	—
(θ=30°)		39.0	0.08	−34.3	37.65	−1.81
		41.4	0.10	107.4	41.70	−1.77
		42.1	0.06	90.2	—	—
		46.0	0.06	−14.8	—	—
		48.3	0.06	−117.3	—	—
2,2′-Bipyridyl	$^1B \leftarrow {}^1A$	33.4	0.74	−62.9	34.80	−3.10
di-cation	$^1A \leftarrow {}^1A$	41.1	0.02	14.1	38.70	−0.60
(θ=40°)	$^1A \leftarrow {}^1A$	43.5	0.01	−23.3	41.80	−0.98
	$^1B \leftarrow {}^1A$	44.1	0.01	−33.6	—	—
	$^1A \leftarrow {}^1A$	46.3	0.03	−32.9	—	—

is twice as strong as that of the latter. The observed 1st and 2nd absorption bands are weak as compared with the corresponding bands of the neutral molecule on the whole.

The MCD spectrum of the mono-cation shows negative bands at 33700 and 37600 cm^{-1} and a positive band at 41700 cm^{-1}. The spectral profile of the mono-cation is much complicated as compared with that of the neutral molecule. This may be attributed to the increase in the dihedral angle and the reduction in the molecular symmetry on protonation.

In Table 2 the calculated transition energies, oscillator strengths, and Faraday *B* values for both the trans- and cis-form with a dihedral angle of 30° are listed and compared with experimental values. There appears an appreciable difference between the calculated Faraday *B* values of the cis- and trans-form. The evaluated MCD signs of the 3rd, 4th, and 6th transitions of the trans-form are opposite to those of the corresponding transitions of the cis-form. Since the

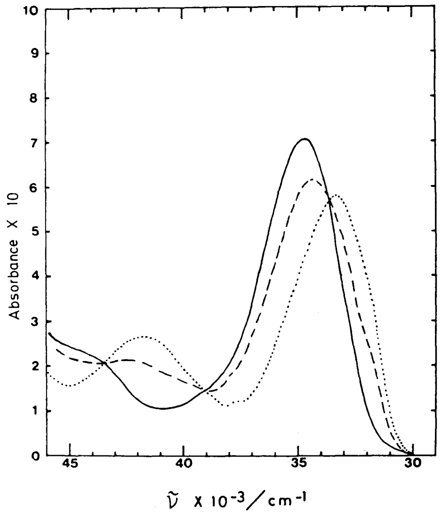

Fig. 3. The absorption spectra of 2,2′-bipyridyl (7.18×10^{-5} M) in sulfuric acid (3.87 M ——; 1.41 M -----; 0.102 M. ·····) at room temperature.

calculated result for the trans-structure is in better agreement with the observation than that for the cis-structure, the mono-cation of 2,2′-bipyridyl is considered to take the trans-configuration. The lowest transition energy of the mono-cation with the trans-structure is predicted to be 28400 cm^{-1}, which is considered to be assigned to the observed absorption band at 33300 cm^{-1} in view of the oscillator strengths.

The calculated Faraday B values and oscillator strengths of the mono-cation in the trans-form with the dihedral angle of 30° are included in Fig. 4 (right).

In Fig. 5 (left) the absorption and MCD spectra of 2,2′-bipyridyl in sulfuric acid of 7.04 M are represented. The absorption spectrum shows an intense band with its maximum at 34600 cm^{-1}. In the higher wave number region a discernible shoulder appears at *ca.* 43300 cm^{-1}. The MCD spectrum exhibits negative extrema at 34800 and 41800 cm^{-1} and a positive peak at 38700 cm^{-1}. The MCD spectral profile of the di-cation differs from that of the neutral molecule and also from that of the mono-cation. Especially, in the energy region of 41000—44000 cm^{-1} both the mono-cation and the neutral molecule exhibit positive MCD's, whereas the di-cation shows a negative band.

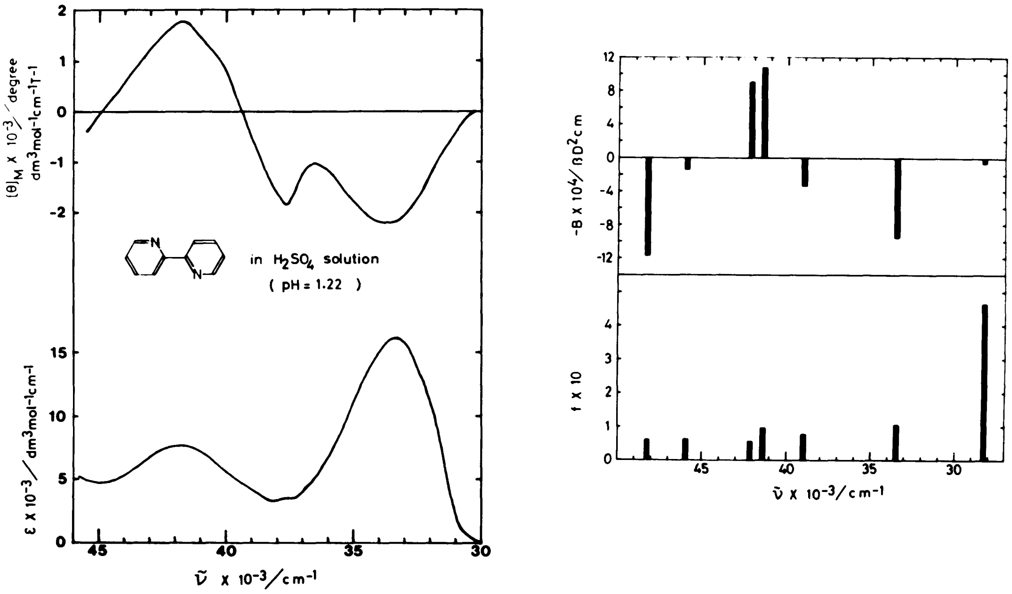

Fig. 4. The observed MCD (left top) and absorption (left bottom) spectra of 2,2′-bipyridyl in sulfuric acid at pH 1.22. Theoretical B values (right top) and oscillator strengths (right bottom) for a trans-structure with $\theta=30°$.

TABLE 2. CALCULATED TRANSITION ENERGIES AND B VALUES OF THE MONO-CATION OF *trans*- AND *cis*-2,2′-BIPYRIDYL $\theta=30°$

Cis-form			Trans-form			Experimental	
$\tilde{\nu}\times10^{-3}$ / cm^{-1}	f	$-B\times10^5$ / $\beta\text{D}^2\text{cm}$	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	f	$-B\times10^5$ / $\beta\text{D}^2\text{cm}$	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	Sign of $[\theta]_\text{M}$
28.4	0.48	−14.1	28.4	0.47	−6.1	33.70	—
33.6	0.07	−88.9	33.5	0.11	−96.0	—	—
38.6	0.12	54.4	39.0	0.08	−34.3	37.65	—
41.4	0.06	−47.4	41.4	0.10	107.4	41.70	+
42.3	0.07	111.1	42.1	0.06	90.2		
46.0	0.07	46.7	46.0	0.06	−14.8		—
48.5	0.04	−143.6	48.3	0.06	−117.3		—

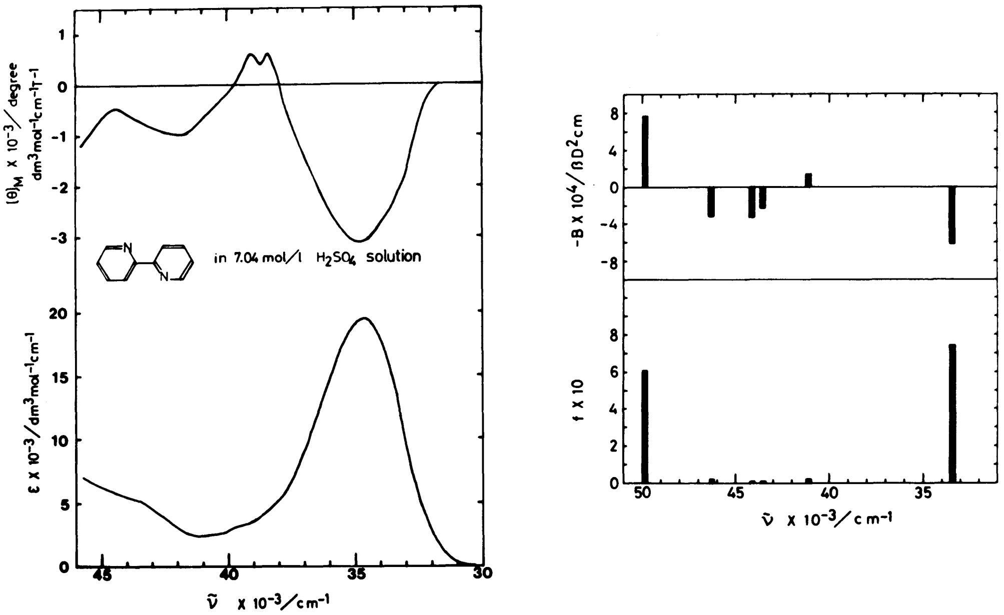

Fig. 5. The observed MCD (left top) and absorption (left bottom) spectra of 2,2′-bipyridyl in sulfuric acid of 7.04 M. Theoretical B values (right top) and oscillator strengths (right bottom) calculated for a trans-structure with θ=40°.

Table 3. Angular dependence of calculated transition energies and B values of the di-cation of 2, 2′-bipyridyl

	0°			10°			20°		
	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	f	$-B\times10^5$ / βD^{2}cm	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	f	$-B\times10^5$ / βD^{2}cm	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	f	$-B\times10^5$ / βD^{2}cm
I	31.5	0.83	−69.1	31.6	0.83	−68.7	32.0	0.81	−67.6
II	40.8	0.00	0.0	40.8	0.00	0.9	41.0	0.01	3.7
III	43.0	0.15	−54.9	43.0	0.02	−61.1	43.3	0.01	−765.4
IV	43.2	0.00	0.0	43.2	0.00	6.0	43.3	0.01	709.8
V	46.2	0.00	0.0	46.2	0.00	−2.1	46.2	0.01	−8.5

	30°			40°			Experimental	
	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	f	$-B\times10^5$ / βD^{2}cm	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	f	$-B\times10^5$ / βD^{2}cm	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	$-B\times10^5$ / βD^{2}cm
I	32.6	0.78	−65.7	33.4	0.74	−62.9	34.8	−78.8
II	41.1	0.01	8.4	41.1	0.02	14.1	38.7	8.1
III	43.4	0.01	−34.7	43.5	0.01	−23.3		
IV	43.6	0.01	−21.8	44.1	0.01	−33.6	41.8	—
V	46.3	0.02	−18.9	46.3	0.03	−32.9	—	—

In Table 3 the calculated Faraday B values and oscillator strengths of the di-cation in a trans-structure are listed along with experimental values. It is clear from Table 3 that the transition energies increase with an increase in the dihedral angle. The 1st, 2nd, and 3rd transitions show characteristic behavior depending on the variation of the dihedral angle. Both the Faraday B value and oscillator strength associated with the 1st transition decrease with an increase in the dihedral angle. On the other hand, those of the 2nd and 5th transitions increase with an increase in the dihedral angle, and are close to zero when θ=0°. The sign of the Faraday B values associated with the 2nd (38700 cm^{-1}) MCD band is calculated to be positive and assigned to the 2nd transition.

From comparison of the theoretical with experimental results, it is concluded that the di-cation of 2,2′-bipyridyl takes a structure twisted by 30—40° around the central bond. The calculated results for the di-cation with a dihedral angle of θ=40° are schematically represented in Fig. 5 (right) and summarized in Table 1. They are considered to be in good agreement with the experimental results.

It seems clear from the above discussion that the di-cation has a comparatively large dihedral angle, and accordigly that the conjugation between two pyridinium rings must be small. This is in contradiction with the inference by Nakamoto[4] and Borgen *et al.*[6] that the di-cation of 2,2′-bipyridyl has a planar structure.

4,4′-Bipyridyl and Its Cations. The UV absorption spectra of 4,4′-bipyridyl in acidic media at pH values between 2.06 and 6.97 are illustrated in Fig. 6. In basic conditions as well as in most organic solvents, 4,4′-bipyridyl exhibits an absorption at 42000 cm^{-1} characteristic of the neutral species.

On the other hand, in acidic solutions at pH<2.06, the UV absorption spectrum of 4,4′-bipyridyl exhibits the same spectral feature as the dotted line in Fig. 6 indicates. Accordingly, the UV absorption spectrum illustrated with the solid line in Fig. 6 is due to the neutral molecule and the one with the dotted line is ascribed to the di-cation.

The absorption and MCD spectra of 4,4′-bipyridyl in cyclohexane are represented in Fig. 7 (left). The negative MCD band at 42500 cm^{-1} corresponds to the absorption at 42500 cm^{-1}. The absorption shoulder at about 37500 cm $^{-1}$ exhibits positive MCD. The MCD spectral profile of 4,4′-bipyridyl in cyclohexane is thus similar to that of substituted biphenyls with electron-attracting groups at the para-positions.

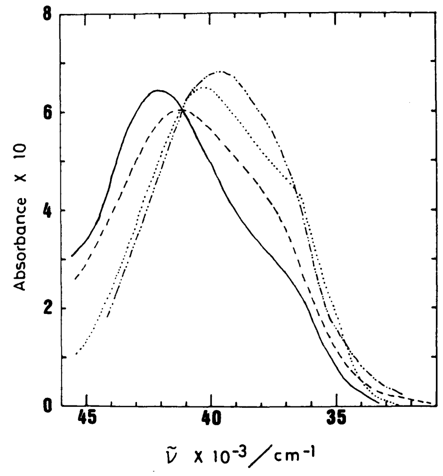

Fig. 6. The absorption spectra of 4,4′-bipyridyl (8.46×10^{-5} M) in sulfuric at pH 2.04 (······), 3.20 (-·-·-·-·-), 5.13 (-----), and 6.97 (——).

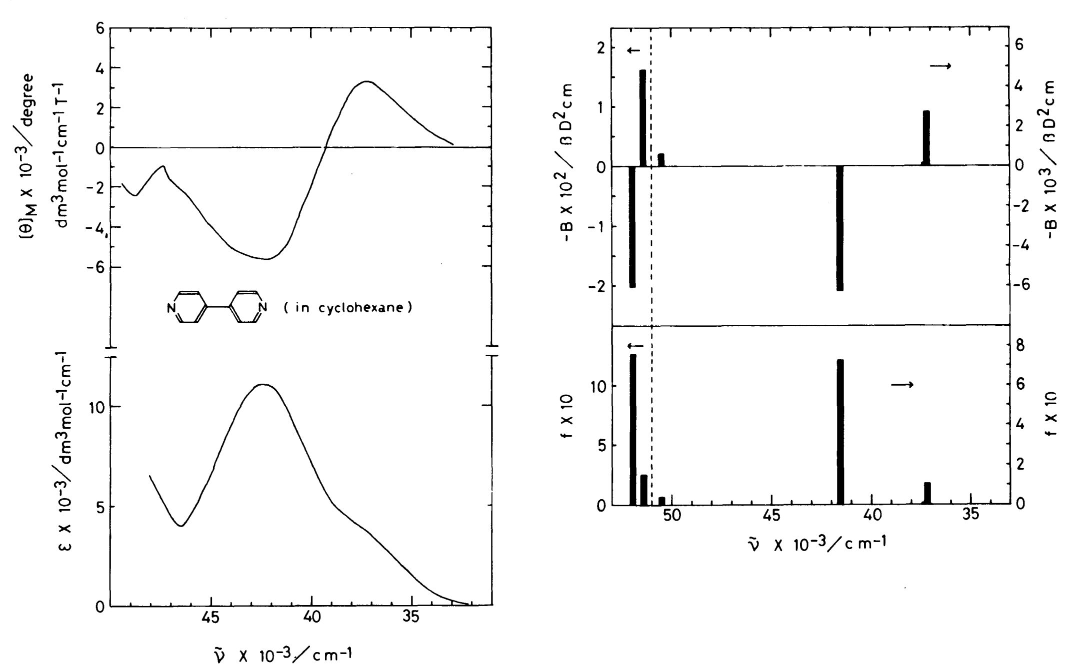

Fig. 7. The observed MCD (left top) and absorption (left bottom) spectra of 4,4′-bipyridyl in cyclohexane at room temperature. Theoretical B values (right top) and oscillator strengths (right bottom) calculated at θ=30°.

TABLE 4. THEORETICAL TRANSITION ENERGIES ($\tilde{\nu}$), OSCILLATOR STRENGTHS (f), AND B VALUES (B) OF 4,4′-BIPYRIDYL

Compound	Theoretical				Experimental	
	Symmetry	$\tilde{\nu}$×10^{-3} cm^{-1}	f	$-B$×10^5 D^{2}cm	$\tilde{\nu}$×10^{-3} cm^{-1}	$[\theta]_M^{max}$×10^{-3}
4,4′-Bipyridyl (θ=30°)	$^1B_2 \leftarrow {}^1A$	37.2	0.11	27.5	37.31	3.21
	$^1B_1 \leftarrow {}^1A$	37.2	0.01	2.0	—	—
	$^1B_3 \leftarrow {}^1A$	41.6	0.73	−62.5	42.46	−5.62
	$^1A \leftarrow {}^1A$	49.9	forb.	0.0	—	—
	$^1B_1 \leftarrow {}^1A$	50.5	0.04	6.6	—	—
4,4′-Bipyridyl di-cation (θ=30°)	$^1B_1 \leftarrow {}^1A$	36.5	0.04	3.1	—	—
	$^1B_2 \leftarrow {}^1A$	36.8	0.47	45.7	35.70	7.16
	$^1B_3 \leftarrow {}^1A$	40.4	0.59	−79.1	40.30	−11.00
	$^1B_1 \leftarrow {}^1A$	48.2	0.00	−1.1	—	—
	$^1B_2 \leftarrow {}^1A$	48.4	0.06	−14.6	—	—
	$^1A \leftarrow {}^1A$	48.8	forb.	0.0	—	—

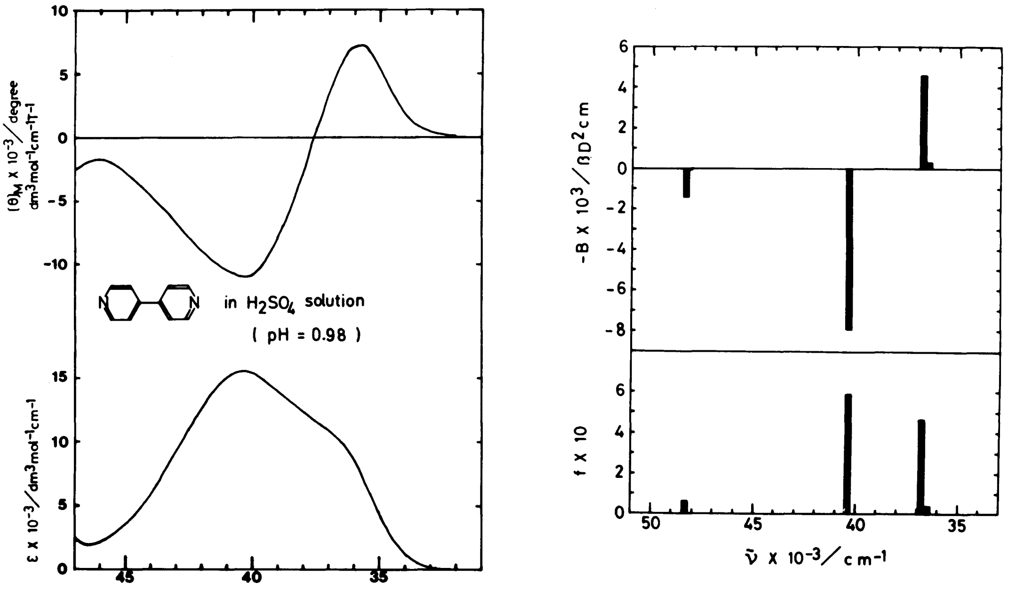

Fig. 8. The observed MCD (left top) and absorption (left bottom) spectra of 4,4′-bipyridyl in sulfuric acid at pH 0.98. Theoretical *B* values (right top) and oscillator strengths (right bottom) calculated at θ=30°.

The Faraday *B* values and oscillator strengths of 4,4′-bipyridyl where the dihedral angle is assumed to be 30° are indicated in Fig. 7 (right). The agreement between experiment and theory is fairly good with respect to the sign, relative intensity, and transition energy. Accordingly, the dihedral angle of 4,4′-bipyridyl may be considered to be about 30°, larger than that of biphenyl in solution which has been found to be 20°.[15] The difference in dihedral angle between 4,4′-bipyridyl and biphenyl may be ascribed to the nitrogen atoms being incorporated in the biphenyl skeleton in the former so as to localize electrons on its para-positions. This leads to a less conjugation between the two rings. Then, 4,4′-bipyridyl exists in a more twisted form than biphenyl, although the repulsion among the ortho-protons seems to be nearly equal in both the cases.

The calculated result for 4,4′-bipyridyl is summarized in Table 4. The 1st and 2nd MCD bands of 4,4′-bipyridyl are assigned to the predicted $^1B_2 \leftarrow {}^1A$ and $^1B_3 \leftarrow {}^1A$ transitions, respectively. The assignment is identical with that for bipyridyl.[14] The absorption and MCD spectra of 4,4′-bipyridyl in sulfuric acid at pH 0.98 are represented in Fig. 8 (left). In the UV spectrum an absorption maximum is observed at 40300 cm^{-1} with a shoulder at about 36000 cm^{-1}. The MCD spectrum exhibits a positive band at 35700 cm^{-1} and a negative one at 40300 cm^{-1}. The intensity of the latter is greater than that of the former. Although the absorption and MCD extrema exhibit a red-shift in comparison with those of the neutral molecule, the di-cation of 4,4′-bipyridyl shows a similar spectral profile to the neutral molecule as a whole.

The calculated result for the di-cation of 4,4′-bipyridyl with θ=30° is included in Fig. 8 (right). It is found that the theoretical result is rather insensitive to the variation of the dihedral angle. The calculated result is summarized and listed in Table 4. The 1st, 2nd, and 3rd $\pi^* \leftarrow \pi$ transitions of the di-cation are calculated to be $^1B_1 \leftarrow {}^1A$, $^1B_2 \leftarrow {}^1A$, and $^1B_3 \leftarrow {}^1A$, respectively, of which transitions $^1B_2 \leftarrow A$ and $^1B_3 \leftarrow {}^1A$ are assigned to the 1st and 2nd MCD bands.

Concluding Remarks

Bipyridyls exhibit characteristic spectra depending on the position of the nitrogen atoms and also on protonation. The observed absorption and MCD spectra are considered to have been reproduced fairly well by a theoretical calculation based on the PPP method, since the agreement between theory and experiment is acceptable in view of the approximation employed.

Calculated absorption and MCD spectra were compared with the observed spectra to get dihedral angles of 30—40° for di-cations of 2,2′- and 4,4′-bipyridyl. In the present work the dihedral angle of 2,2′- and 4,4′-bipyridyl have been estimated to be 0° and 30°, respectively.

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