Electronic Spectra of Phenanthrolinediones, Phenanthrolinones, Bipyridinediones, and Amino-Substituted Phenanthrolines

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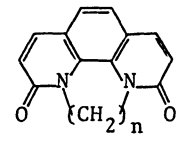
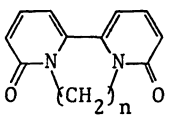
The electronic spectra of three types of 1,10-phenanthroline derivatives having different π-conjugated systems, phenanthrolinedione, phenanthrolinone, and the parent phenanthroline, showed characteristic patterns easily distinguished from each other. Analogous spectral patterns were noted in amino-substituted 1,10-phenanthrolines, and the protonated structures of these compounds were characterized on the basis of such spectral features.

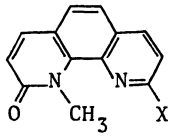
Recently we reported on the preparation of *N,N'*-annelated phenanthrolinedione **1a** and **1b**, and bipyridinedione **2a** and **2b**, as potential precursors of the corresponding dichloro derivatives of 1,10-phenanthroline (phen) and 2,2'-bipyridine (bpy), respectively.[1] These diones seem to be also attractive compounds as "extended" α-pyridinones. From these viewpoints, we investigated in detail the electronic spectra of **1a**, **1b**, **2a**, **2b**, well-known phenanthrolinone **3a**,[2] **3b**,[3] and nonannelated bipyridinedione **2c**.[4] The electronic spectra of **1a,b** and **3a,b** were largely different from that of the parent phen and from each other, whereas there were small differences in spectral patterns between **2a**—**c** and the parent bpy. It was suggested that the characteristic of spectral patterns should be a good means in identifying the formal π-conjugated systems in phen derivatives regardless of the shifts in absorption maxima.[5] Further, spectral patterns analogous to those of **1** and **3** were observed in the spectra of protonated forms of amino-substituted phens, 1,10-phenanthroline-2,9-diamine (**4**)[3] and 1,10-phenanthrolin-2-amine (**5**).[6] The protonated structures of **4** and **5** were characterized by examining the spectral patterns.



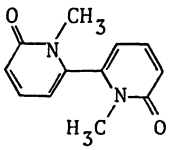
1: **a**; n=2
b; n=3



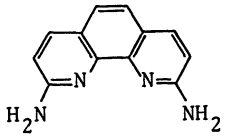
2: **a**; n=2
b; n=3



3: **a**; R=H
b; R=Cl



2c



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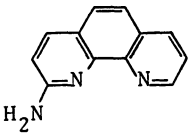

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Results and Discussion

Electronic Spectra of Phenanthrolinones and Bipyridinones. The electronic spectra of phen, a phenanthrotinone **3a**, and a phenanthrolinedione **1a** in 250—450 nm region are shown in Fig. 1. A strong π–π^* transition band (β'-band) and two additional bands of

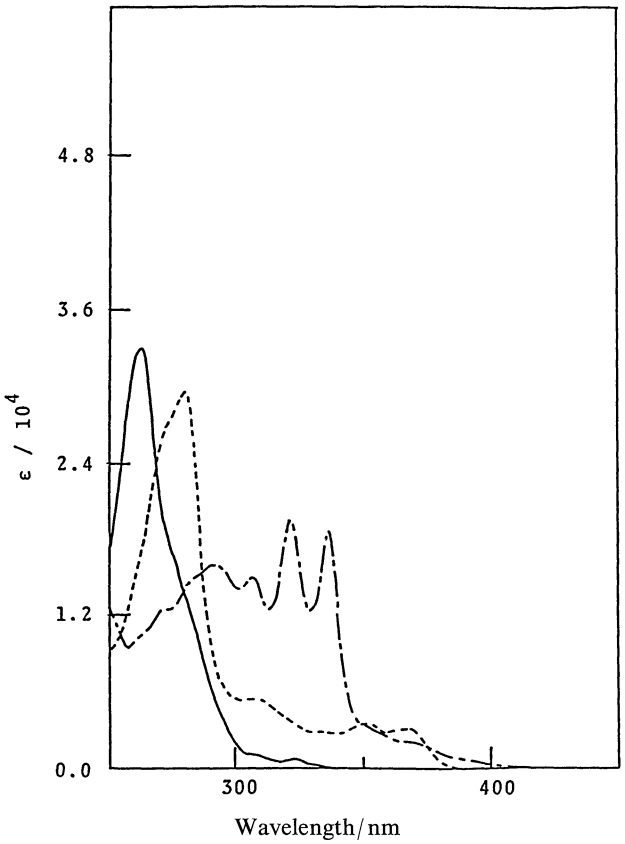


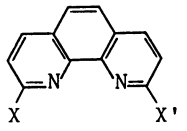
Fig. 1. Electronic spectra of (——): phen, (-----): **3a**, and (— - —): **1a** in methanol.

much lower intensity at longer wavelengths (p-band and α-band) appeared in the spectrum of phen.[7] Noticeable differences are observed between the spectrum of **3a** and that of phen, i.e., three clear peaks of much higher intensity than that of p- and α-bands (λ_{max}=308, 352, and 369 nm, with $\log\varepsilon_{max}$=3.74, 3.55, and 3.50, respectively) appeared in the spectrum of **3a**. The spectrum of **1a** is quite different from those of both phen and **3a**, i.e., four peaks of similar intensities (λ_{max}=271, 291, 307, 322, and 337 nm, with $\log\varepsilon_{max}$=4.10, 4.21, 4.18, 4.29, and 4.27, respectively) are observed instead of the β'-band.

The spectral patterns of the parent phen are not affected by simple substituents such as amino,[3,6] chloro,[2,3] and methoxy groups[8,9] at 2- and 9-positions. The only noticeable influences caused by substituents were the red shifts according to the nature and number of substituents and appearances of sub-peaks in β'-bands of disubstituted derivatives, **7** and **9** (Table 1).

The electronic spectra of another phenanthrolinone **3b**[3] and another phenanthrolinedione **1b** along with **3a** and **1a** are depicted in Fig. 2. The chloro substituent in **3b** caused a small red shift compared with **3a**, in a similar manner to the chloro substituent in **6**. Exchange of the ethano-bridge in **1a** by a propano-bridge in **1b** also resulted in a small red shlft.[1,10] Nevertheless, the spectral patterns of **3b** and **1b** are quite similar to those of the corresponding compounds having the same formal π-conjugated systems, **3a** and **1a**, respectively. These results indicate that the characteristic spectral patterns of phen, **3a**, and **1a** reflect the individual π-conjugated systems rather than the substituent effects.

This speculation was supported further by spectral measurement of **1a** in strong acidic media. In concentrated sulfuric acid, the absorbances at wavelengths shorter than 300 nm were increased to a level of the β'-bands (Fig. 3). Since two different sets of isosbestic points appeared successively during spectrometric titration with sulfuric acid (Fig. 3-A and -B), stepwise protonation to the two oxygen atoms in **1a** should take place in strong acidic media, forming **1'a** and **1''a** (Scheme 1). The diprotonated form **1''a** may exist in resonance with **1'''a**, whose π-conjugated system is the same as that of phen.



6; X=Cl, X'=H
7; X=X'=Cl
8; X=OMe, X'=H
9; X=X'=OMe

Table 1. Absorption Maxima of β'-Bands of phen Derivatives in Methanol

Compound	λ_{max}/nm ($\log\varepsilon_{max}$)
5	287 (4.45)
4	309 (4.43)
6	268 (4.63)
7	273 (4.54), 293 (4.26)
8	274 (4.53)
9	281 (4.47), 294 (4.34)

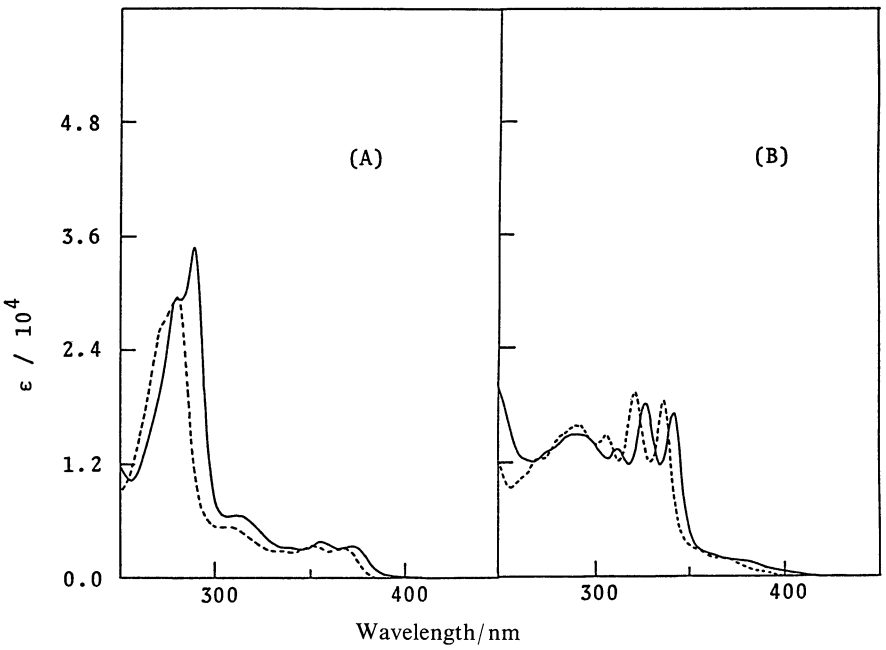


Fig. 2. Electronic spectra of (A) (——): **3b** and (------): **3a**, and (B) (——): **1b** and (– – –): **1a** in methanol.

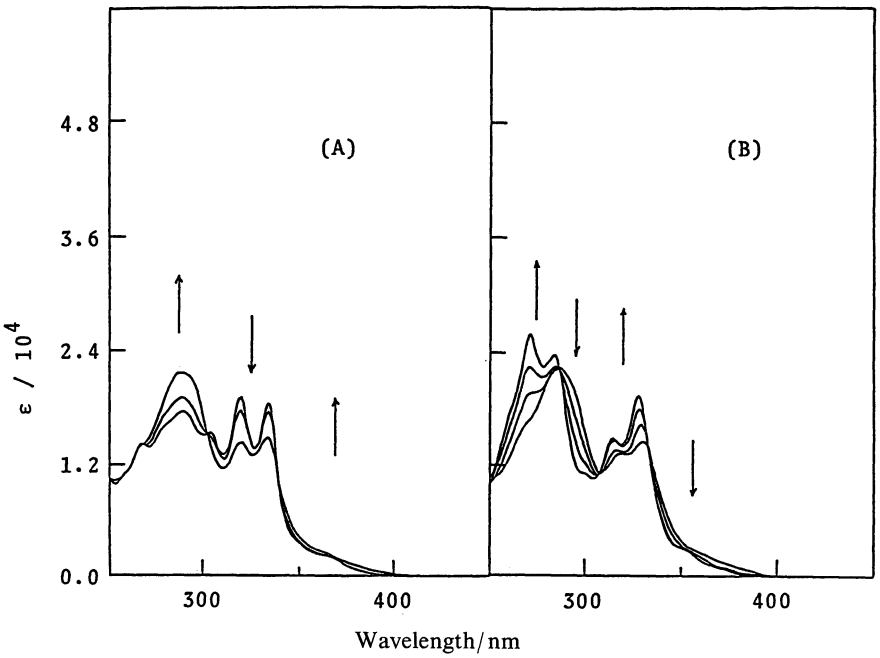
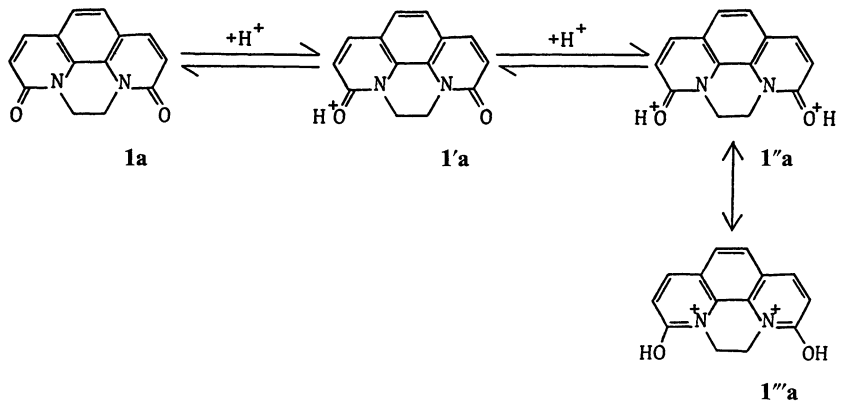


Fig. 3. Spectral change of **1a** by increasing concentration of sulfuric acid. Concentrations of sulfuric acid; (A): 0, 10, and 20%, (B): 30, 40, 50, and 90%.



Scheme 1.

The electronic spectra of bipyridinediones **2a**—**c** in 250—450 nm region are displayed in Fig. 4. It is well-known that a strong π–π^* transition band of the parent bpy (β'-band,[11] λ_{max}=280 nm[12]) appears in this region. Analogous bands indeed appear in the spectra of **2a**—**c**. The large red shifts of absorption maxima from that of the parent bpy (93, 63, and 36 nm for **2a**, **2b**, and **2c**, respectively) are noted, which should be attributed to changes in the π-conjugated systems.[5] Large shifts of absorption maxima can take place also by rotation of the interannular bond,[1,13,14] i.e., large blue shifts occur in the spectra of twisted bipyridinediones, **2b** and **2c** (30 and 57 nm, respectively), compared with the planar one, **2a**. Thus we should be careful in identifying the π-conjugated systems of bpy derivatives in terms of the shifts of absorption bands.[5,13]

Amino-Substituted Phen's and Their Protonated Structures. Though the amino substituents at 2- and 9-positions in **4** and **5** do not affect the spectral pattern of phen (see above), protonation to these compounds effected large changes in the spectral pattern. The electronic spectra of amino-substituted phen's, **5** and **4**, and their protonated forms are shown in Fig. 5. A one-step protonation was detected by spectrometric titration of **5** within a pH range of 10 to 0 (pK_a=6.9[15]). A large change in the spectral pattern took place by the protonation, i.e., several prominent peaks appeared at longer wavelengths (Fig. 5-A). In the case of **4**, two-step protonations were observed within a pH range of 10 to 0 (pK_a=7.9 and 2.1[16]). Though the change in the spectral pattern was marginal by the first protonation, it was fairly drastic by the second protonation (Fig. 5-B). In

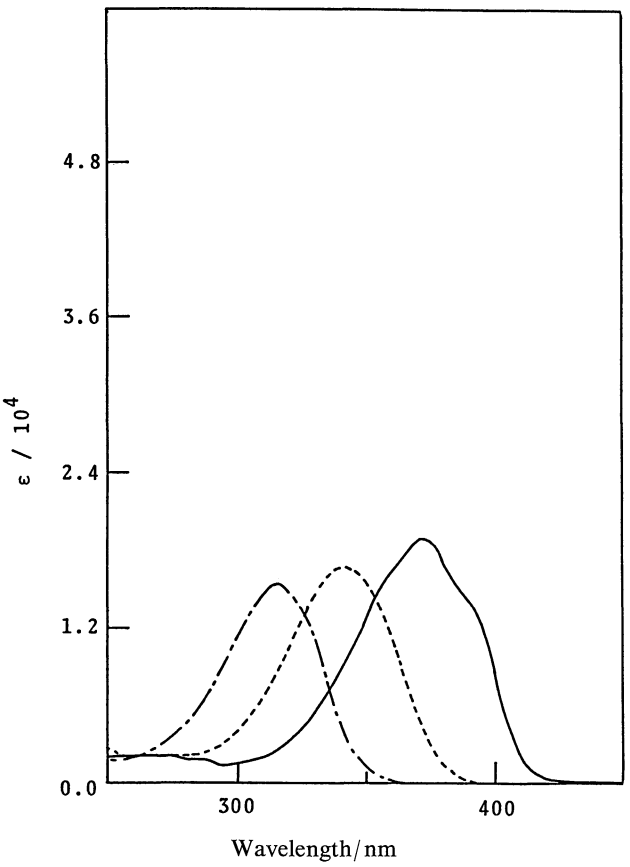
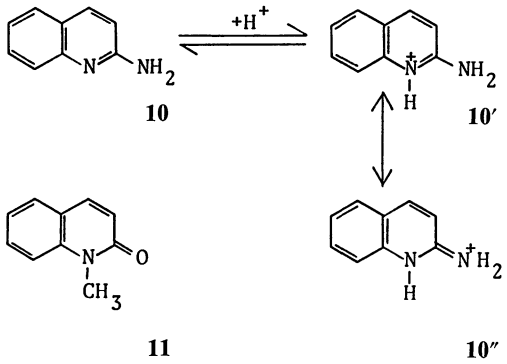


Fig. 4. Electronic spectra of (——): **2a**, (----): **2b**, and (— - —): **2c** in methanol.

contrast, only the shifts of the β'-band were noted by the protonation to phen.[17] Since the spectral changes of **4** and **5** are reversible, these changes do not reflect degradation reactions. A comparison between these spectra and some spectra discussed above (Fig. 6) shows that the spectral pattern of the monoprotonated **5** is quite similar to that of **3a** (Fig. 6-A), and that the spectral patterns of diprotonated form of **4** resemble that of phenanthrolinedione **1a**, though the sharpness of each peak is reduced to some extent (Fig. 6-B).

Analogous spectral similarity was observed between simpler heteroaromatic compounds, 2-quinolinamine **10** and 1-methyl-2(1*H*)-quinolinone **11**. A one-step protonation took place in **10** within a pH range of 10 to 0 (pK_a=7.3).[18] The electronic spectra of **10** in free and monoprotonated forms and **11** in a 250—450 nm region are illustrated in Fig. 7. The single peak appearing in



Scheme 2.

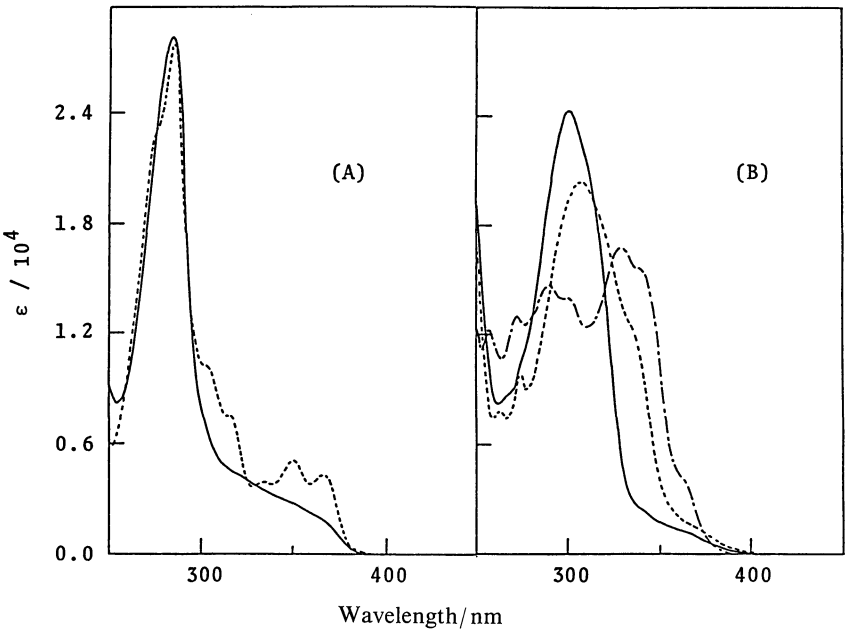


Fig. 5. Electronic spectra of (A) **5** and (B) **4** in aqueous buffer solution; (——): free form, (----): monoprotonated form, and (— - —): diprotonated form.

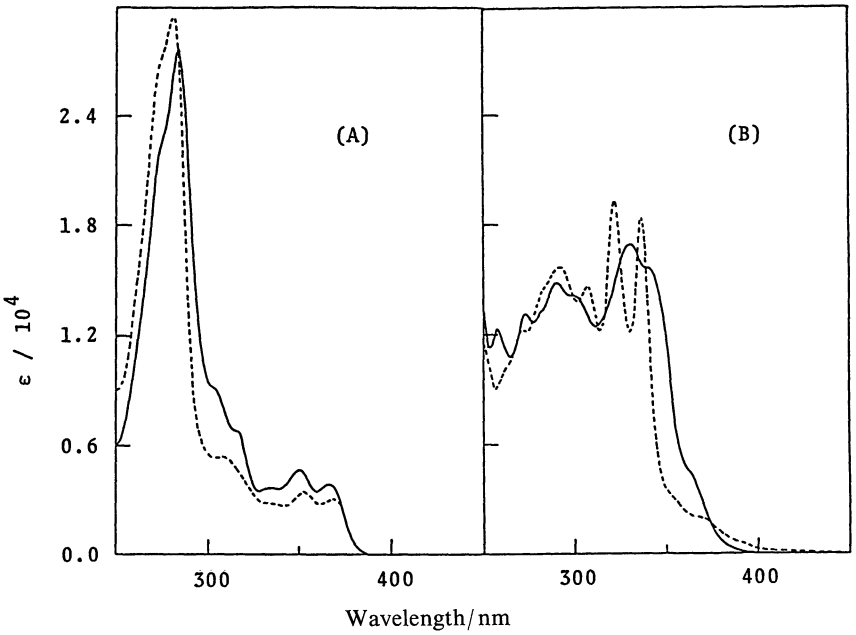


Fig. 6. Spectral comparison of amino-substituted 1,10-phenanthrolines in protonated forms and the corresponding phenanthrolinones; (A) (——): monoprotonated form of **5** in aqueous buffer solution and (------): **3a** in methanol, (B) (——): diprotonated form of **4** in aqueous buffer solution and (– – –): **1a** in methanol.

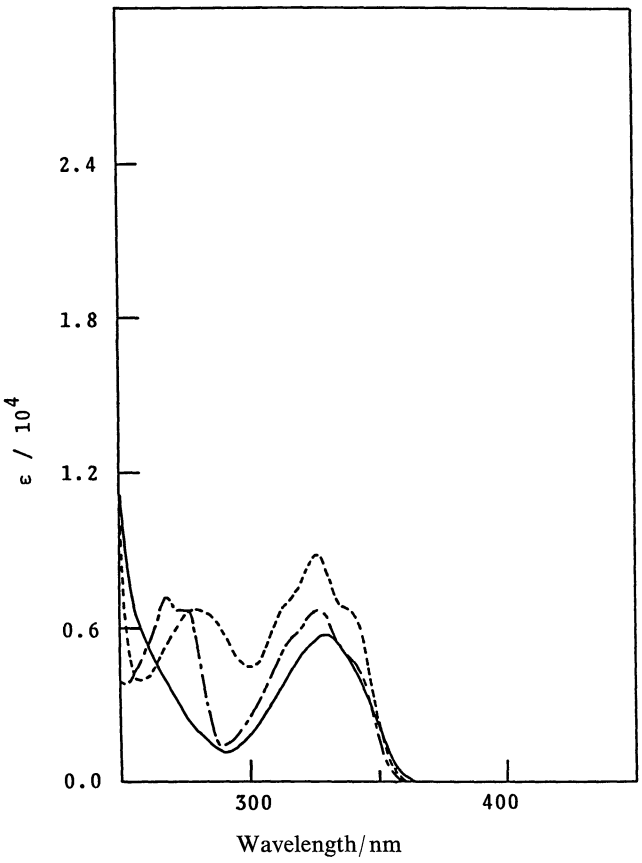
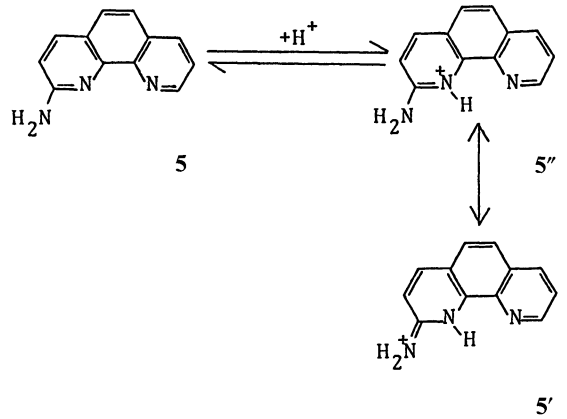


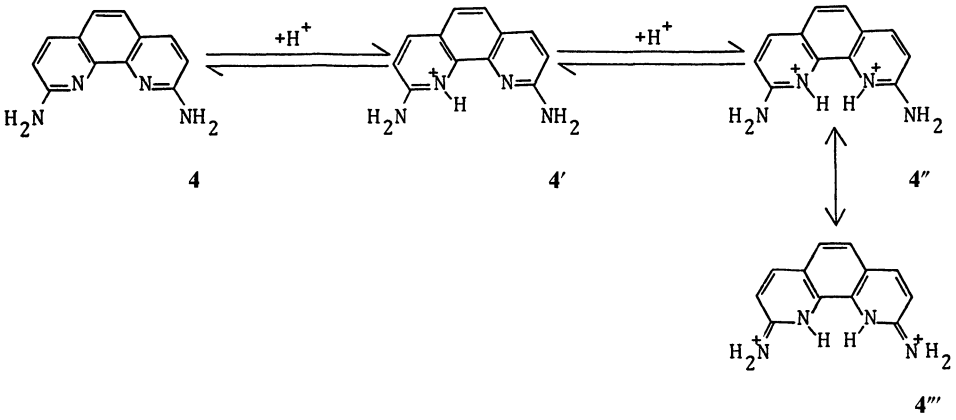
Fig. 7. Electronic spectra of (——): free form of **10** in aqueous buffer solution, (------): monoprotonated form of **10** in aqueous buffer solution, and (— – —): **11** in methanol.

the spectrum of the free form of **10** splitted into two major peaks by protonation. The spectral pattern of monoprotonated **10** was similar to that of **11**. Protonation to **10** took place on the ring nitrogen to form **10′**, because the ring nitrogen of amino-substituted pyridines has much higher basicity than the amino nitrogen.[12,19] There is a large contribution of the resonance structure **10″** in **10′**.[18,20] The spectral similarity of monoprotonated **10** and **11** should be attributed to the similarity of the π-conjugated systems between **10″** and **11** (Scheme 2).

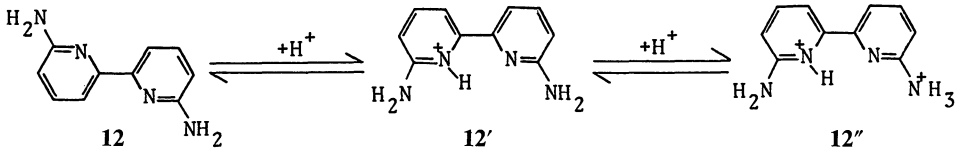
The spectral similarity between monoprotonated **5** and **3a**, and between diprotonated **4** and **1a**, can be rationalized by the same argument. The initial proton-



Scheme 3.



Scheme 4.



Scheme 5.

ation to **5** takes place on the nitrogen in 1-position rather than in 10-position[6] forming **5'**, because the amino substituent at α-position of the pyridine ring significantly increases the basicity of the neighboring ring nitrogen.[12,18–20] There would be a large contribution of the resonance structure **5''**, which is a conjugated system quite similar to that of **3a** (Scheme 3). For the same reason, the initial protonation to **4** should take place at one of the ring nitrogens, forming **4'**. The second protonation should take place at the other ring nitrogen to form **4''**, which has a resonance structure **4'''**. The formal π-conjugated system of **4'''** is quite similar to that of **1a** (Scheme 4). If the second protonation should take place on one of the amino nitrogens, one cannot draw a π-conjugated system similar to that of **1a**. On the other hand, the spectral pattern of monoprotonated form **4'** resembles that of phen rather than that of **3a**. This suggests that the positive charge in **4'** is delocalized not only over the neighboring amino nitrogen but also over the other pyridine ring and its amino substituent, thereby lowering the contribution of the π-conjugated system similar to that of **5''**.

As discussed above, at least judging from the spectral features of phenanthroline derivatives, both the first and second protonation to **4** appear to take place on the ring nitrogens. It is well-known that the second protonation to the ring nitrogens of phen and bpy occurs only in such strong acidic media as concentrated sulfuric acid because of a repulsion between the neighboring protons in diprotonated forms.[17,21] In the present case, however, the second protonation to the ring nitrogen of **4** is apparantly completed at pH 1. Incidentally, the acid-base properties of 2,2'-bipyridine-6,6'-diamine **12**, a bpy analogue of **4**, have been studied by electronic and ^{1}H NMR spectroscopies,[22] and it has been concluded that the second protonation to **12** takes place at the amino nitrogen rather than the ring nitrogen (Scheme 5). Since there were only minor changes in the spectral patterns by protonation to **12**, there should be some uncertainty as to the actual forms for reasons given above with respect to **2a**—**c**.

The absorption maxima and the ^{1}H NMR chemical

Table 2. Spectral Comparison of **4** and **12** with the Parent phen and bpy

Compound	λ_{max}/nm[a]	^{1}H NMR/δ[b] (position)			
4 (A)	309	—	6.81 (3,8)	7.88 (4,7)	7.29 (5,6)
phen (B)	264	9.12 (2,9)	7.77 (3,8)	8.50 (4,7)	7.99 (5,6)
(A)−(B)	45	—	−0.96 (3,8)	−0.62 (4,7)	−0.70 (5,6)
12 (C)	334[c]	—	6.38 (5,5')	7.36 (4,4')	7.36 (3,3')[d]
bpy (D)	280[c]	8.43 (6,6')	7.24 (5,5')	7.72 (4,4')	8.15 (3,3')[d]
(C)−(D)	54	—	−0.86 (5,5')	−0.36 (4,4')	−0.79 (3,3')

a) In methanol. b) In dimethyl-d_6 sulfoxide. c) Ref. 12. d) Ref. 22.

shifts for **4** and **12** are summarized in Table 2 together with those of the parent phen and bpy. At least in acid-free forms, the electron donating effects of amino substituents seem to be very similar in the two compounds, as judged from the red shifts in the electronic spectra and the ^{1}H NMR high field shifts.[23] The second protonation to **12** (pK_a=2.2[22]) might also take place at the ring nitrogen in a similar manner to that of **4** (pK_a=2.1). Systematic investigations are needed, however, to settle this problem.

In conclusion, we demonstrated that the electronic spectra of the three types of phen derivatives, **1a**,**b**, **3a**,**b**, and the parent phen, show neatly different spectral pattern distinguished from each other by visual inspection. This may reflect the differences in the individual π-conjugated systems. Such a feature could be a good means to elucidate the electronic structure and related properties of phen and the corresponding bpy derivatives.

Experimental

Materials. Preparation of 5,6-dihydropyrazino[1,2,3,4-*lmn*][1,10]phenanthroline-3,8-dione (**1a**), 6,7-dihydro-5*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9-dione (**1b**), 6,7-dihydrodipyrido[1,2-*a*:2′,1′-c]pyrazine-4,9-dione (**2a**), 7,8-dihydrodipyrido[1,2-*a*:2′,1′-c][1,4]diazepine-4,10-dione (**2b**), and 2,9-dichloro-1,10-phenanthroline (**7**) was reported elsewhere.[1] The following materials were prepared by literature procedures: 1-Methyl-1,10-phenanthrolin-2(1*H*)-one (**3a**), mp 123—124 °C (lit,[2] 123—124 °C), 9-chloro-1-methyl-1,10-phenanthrolin-2(1*H*)-one (**3b**), mp 153—154 °C (lit,[3] 154—155 °C), 1,10-phenanthroline-2,9-diamine (**4**), mp 296—298 °C (lit, 1[3] 273—275 °C, lit, 2[9] 296—298 °C), 1,10-phenanthrolin-2-amine (**5**), mp 188—192 °C (lit,[6] 187—190 °C), 2-chloro-1,10-phenanthroline (**6**), mp 129—130 °C (lit,[2] 129—130 °C), 2-methoxy-1,10-phenanthroline (**8**), mp 78—80 °C (lit,[8] 74—76 °C), 2,9-dimethoxy-1,10-phenanthroline (**9**), mp 111—113 °C (lit,[9] 110—111 °C), 1,1′-dimethyl-2,2′-bipyridine-6,6′-(1*H*,1′*H*)-dione (**2c**), mp 224—225 °C (lit,[4] 210—211 °C). 1,10-Phenanthroline (phen) and 2-quinolinamine (**10**) were commercially obtained. 1-Methyl-2(1*H*)-quinolinone (**11**) was prepared by a procedure analogous to that for 3a:[2] recrystallyzed from petroleum ether (bp 30—70 °C), mp 71—72 °C (lit, 1[24] 68—69 °C, lit, 2[25] 73—74 °C).

Spectral Measurements. Electronic spectra were recorded on a Shimadzu UV-265FS Spectrophotometer at 20 °C. ^{1}H NMR spectra were measured with a JEOL JNM-FX90Q Spectrometer at room temperature. The buffer solutions used for spectrometric titrations were as follows:[26] weakly basic area, potassium borate buffer; weakly acidic area, acetic acid-sodium acetate buffer; acidic area, HCl–KCl buffer.

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