

ULTRAVIOLET ABSORPTION SPECTRA OF 4-AMINO- AND 4-DIMETHYLAMINO-PYRIDINES: EFFECTS OF CONCENTRATION AND SOLVENT

Chikara Kaneko,* Kazuhiro Shiba, and Harue Fujii

Faculty of Pharmaceutical Sciences, Kanazawa University, Takaramachi, Kanazawa, 920, Japan

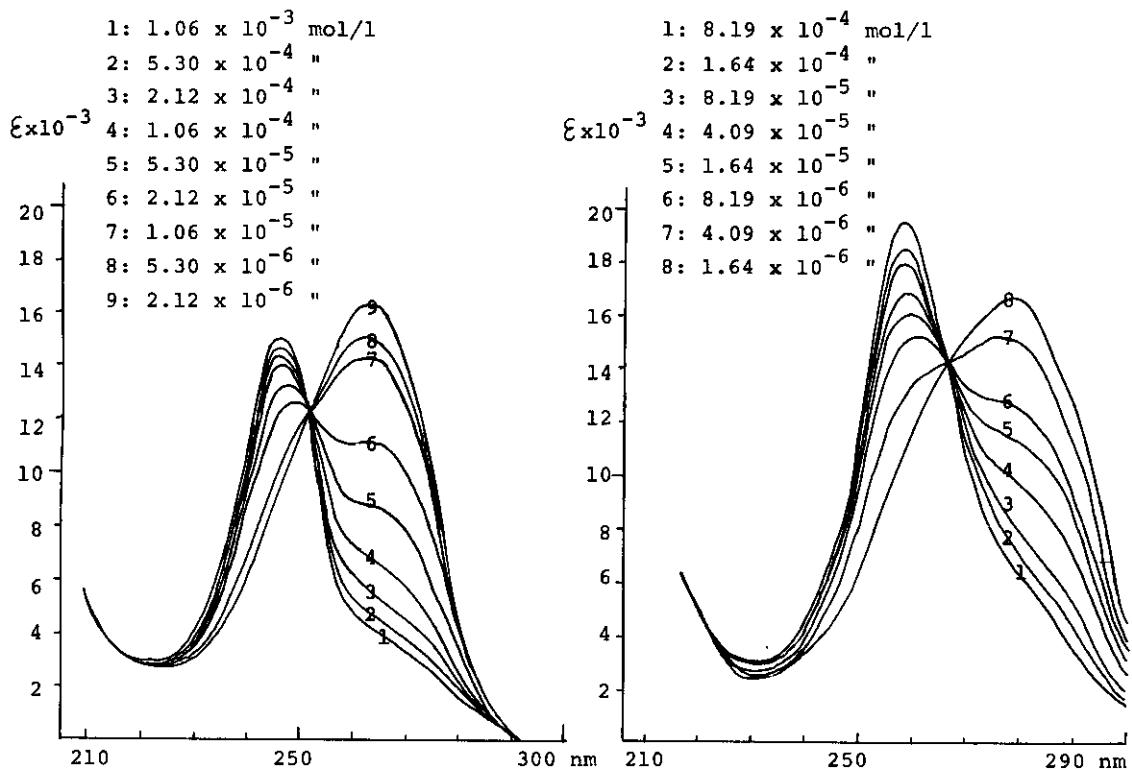
Abstract — The effect of concentration on the UV spectra of 4-aminopyridine and its derivatives in various solvents was studied in the concentration range from 10^{-6} to 10^{-3} M/l. At high concentration, 4-aminopyridines were found to form molecular aggregates (loosely bonded dimers) showing the maxima around 245-260 nm, whose position corresponded to those previously assigned as the 1L_a -band of the monomer. The monomeric form of these pyridines showed a single absorption maximum around 265-280 nm, which had been previously assigned as the 1L_b -band of the monomer.

In the UV spectrum of 4-aminopyridine (I), a low intensity shoulder (around 270 nm) appears on the long wavelength side of the single measurable band (around 240 nm) and the position of the former band is comparable to the single measurable band of the cation and the imine form.¹ These two absorption bands also present in the spectra of the related compounds (e.g., 4-aminopyridines having alkyl substituents either on the amino function or the ring carbon atoms).² The long wavelength band is assigned as 1L_b -band (or α -band) and the shorter one as 1L_a -band (or β -band).³ Assuming that the Lambert-Beer laws were held for all compounds, numerous spectral data (λ_{\max} , ϵ , etc.) were recorded in literature.^{1,2,4} Some theoretical calculations for the prediction of position of these two bands have also been reported.^{1a,5}

The present authors investigated the concentration effect on the absorption spectra of 4-amino- and 4-dimethylaminopyridines (I and II) in various solvents and have found that the Lambert-Beer laws did not hold for these compounds. By the analysis of spectra, the reason for this violation has been clarified due to their

easy dimerization (in this paper, the terms of dimer and dimerization are used for loosely bonded molecular dimer and not for covalently bonded dimer). The object of the present paper is to report these data in detail together with to discuss a possible structure of these dimers.

Examples of the concentration dependence upon the absorption spectra of I and II in methanol are shown in Figs. I and II.* It is clear from these spectral changes that there are two molecular species in the equilibrium, i.e., the monomer and dimer (or its higher aggregate). In order to determine the association number of the aggregate by the method of Zanker,⁶ $\log\{C_0(1-\epsilon/\epsilon_m)\}$ was plotted against $\log\{C_0(\epsilon-\epsilon_n)/\epsilon_m\}$, where ϵ_n and ϵ_m are the extinction coefficients of nth polymer and monomer at the same wavelength. Fig. 3 illustrates these relations obtained for I and II in methanol at room temperature. The straight lines with slope equal to ca. 2 confirm the respective formations of 1:1 complexes (Fig. III).



* UV spectra were measured with Hitachi 320 spectrophotometer and the cell lengths used were 10, 1, and 0.2 cm.

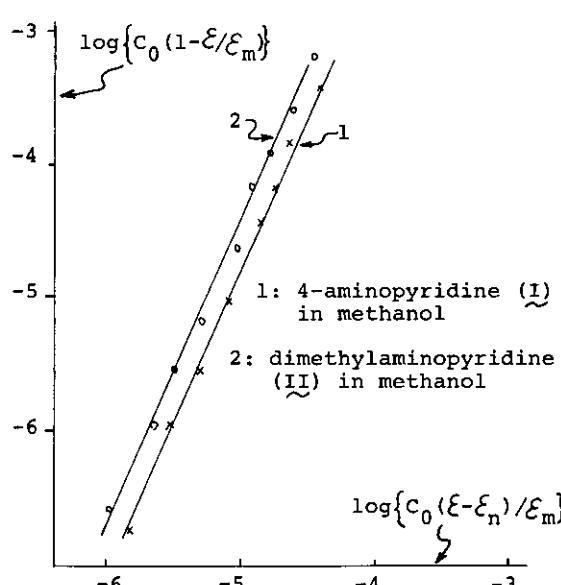


Fig. III. Relations between $\log\{C_0(1-\epsilon/\epsilon_m)\}$ and $\log\{C_0(\epsilon-\epsilon_n)/\epsilon_m\}$.

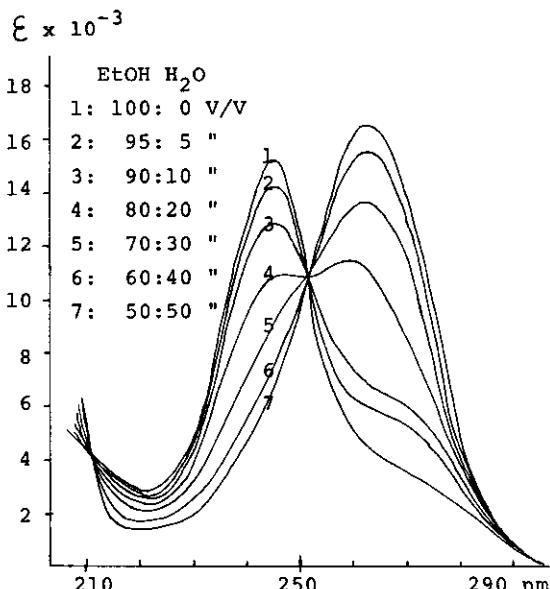
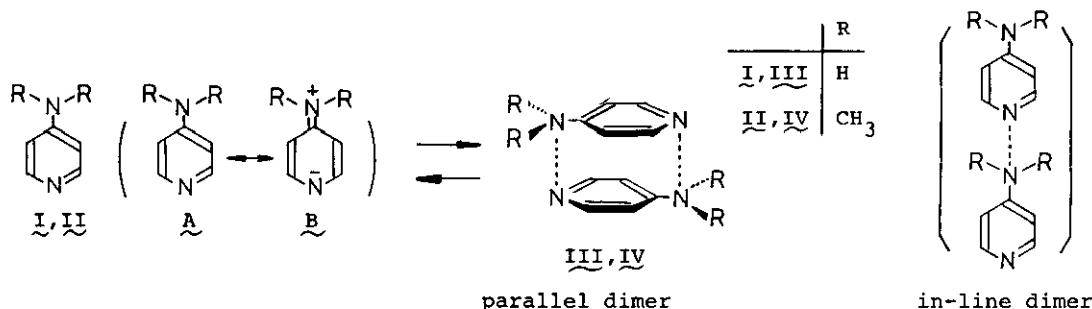


Fig. IV. UV spectra of I in mixtures of ethanol and water (Concentration of I: 5.02×10^{-5} mol/l).

Spectra of I in mixtures of ethanol and water with various proportions are shown in Fig. IV. As compared with the equilibrium between monomer and dimer in methanol, the equilibrium favors monomer in water and dimer in ethanol.

The molecular exciton theory for molecular aggregates predicts that, while the singlet-singlet transition in the parallel dimer is blue shifted, that in the in-line dimer should red shift, with respect to that in the monomer.⁷ Considering the above theory as well as the expected charge separation in the monomer (e.g., B), the parallel dimers (III and IV) formed by dipole-dipole electrostatic attraction between the two monomers are expected for 4-aminopyridines (I and II). The lower association tendency of I in water can also be rationalized on the basis of high hydrogen bonding ability of the solvent relative to methanol or ethanol, because the negative charge on the ring nitrogen atom in the monomer which takes



part in the hydrogen bonding with the solvent would lose its effectiveness in the parallel dimer (III) due to cancellation of the electric charges.

The same phenomena were also observed for 4-methylaminopyridine, 4-aminopyridines substituted with alkyl or chlorine functions at the ring carbon atoms, and even dehydro- α -matrinidine (1-methyl-4,5,6,8,9,10-hexahydropyrido[3,4,5-i,j]quinolizine),^{8,9} and hence seem to be quite common for 4-aminopyridine derivatives.

The present findings lead to at least two important conclusions: 1) the data concerned with the UV spectra of 4-aminopyridines so far reported in literature¹⁻⁵ are not reliable, and 2) the conventional classification of the $\pi-\pi^*$ bands of 4-aminopyridines as well as the calculation methods for them^{1a,5} must be reevaluated.

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8. The UV spectra of this highly substituted 4-aminopyridine also exhibited concentration dependence in methanol, showing the maximum of the monomer at 293 nm and that of the dimer at 273 nm. We thank Prof. Shigenobu Okuda, Institute of Microbiology, University of Tokyo, for the gift of the sample.
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