The Stretching Vibration of N-H Link of 2-Aminopyridine

By Reisuke SODA

(Received February 6, 1957)

Introduction

The Watson-Crick model on the molecular structure of deoxyribonucleic acid[1] has been regarded as an excellent picture but it leaves some doubts about its certainty. One of them is concerned with the tautomerism of base. The present study is undertaken in order to provide confirmatory data for the tautomerism of 2-aminopyridine as the simplest base.

Whether 2-aminopyridine exists in the amino form or in the imino form has been discussed for years[2-4] and now many

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[1] J. D. Watson and F. H. C. Crick, *Nature*, **171**, 737, 964 (1953); F. H. C. Crick and J. D. Watson, *Proc Roy. Soc., London*, **A223**, 80 (1954).

[2] E. A. Steck and G. W. Ewing, *J. Am. Chem. Soc.*, **70**, 3397 (1948); L. C. Anderson and N. V. Seeger, ibid., **71**, 340 (1949).

[3] A. E. Tschitschibabin, R. A. Konowalowa and A. A. Konowalowa, *Chem. Ber.*, **54B**, 814 (1951).

[4] S. L. Angyal and C. L. Angyal, *J. Chem. Soc.*, **1952**, 1461.

results support the amino form of this compound. Experimental results obtained from infrared absorption spectra[5,6] also support the amino form but their discussions are limited on the absorption band position of the stretching vibration and the deformation vibration of the N-H link; consequently their conclusions appear to be qualitative and unsatisfactory. In this report the observation covers not only the band frequency but also the integrated intensity; moreover a reliable conclusion for the amino form is obtained.

Experimental

The Perkin-Elmer model 112 spectrophotometer with a lithium fluoride prism was used[7], but the measurement on toluidines was carried out with a calcium fluorite prism. The theoretically calculated slit widths were 5 cm.$^{-1}$ at 3400 cm.$^{-1}$ for the calcium fluorite and 3 cm.$^{-1}$ for the lithium fluoride. These values were about one fifth of each band width, but the actual slit widths were considered to be wider than the aforementioned values[8]. The cell thickness was about 10 mm. and the concentration of solution was taken from 0.02 moles per liter to 0.001, in order to put optical densities in the range of 0.8 to 0.2. The range of the observed wave number was from 3700 cm.$^{-1}$ to 3000 cm^{-1}.

The c.p. carbon tetrachloride was used as the solvent, which was distilled after drying with phosphorous pentoxide. The reagents were purified as follows. Aniline was distilled at 90°C/16 mmHg and pyrrole at 130°C. Indole[9] was recrystallized from ethanol-water solvent. 2-Aminopyridine was recrystallized from ligroine with petroleum ether, one part of which was further purified by vacuum distillation. Only c.p. toluidines were used without purification.

N-Methyl-2-pyridonimine was synthesized from methyl iodide and 2-aminopyridine by the method of Tschitschibabin et al.[3]; after recrystallization of the product, 2-aminopyridine methiodide from alcohol, its aqueous solution was treated with fresh silver oxide obtained from silver nitrate and sodium hydroxide and the filtrate was concentrated *in vacuo*. The final viscous greenish liquor was distilled at 100°C/12 mmHg. The distillate was slightly yellow and viscous, and turned to a brownish-red substance which became more viscous in the air. Therefore the distillation was carried out at every measuremnt. The purities of reagents were justified by comparison of observed spectra with those given in the literatures.

The molar extinction coefficient and the integrated intensity of the absorption band were obtained with the usual extrapolation method[8]. But in the case of a band overlapping, the following method is preferable. First, the total area of two bands is measured with planimeter. Next, the values of the products, 'the peak optical density times the half-band width' for both the absorption bands are obtained respectively and the ratio of these values is calculated. Then the total area is proportionally divided into two bands according to this ratio and the area of each band determined.

The units of those values are as follows:

$$E = (1/cl)\log_{10}(I_0/I)\,\text{cm.}^2\cdot\text{mol.}^{-1}$$

$$A = (1/cl)\int \ln(I_0/I)\,d\nu\,\text{cm.}^2\cdot\text{molecule}^{-1}\cdot\text{sec.}^{-1}$$

Where c is the concentration of the solution in moles per cc. for the molar extinction coefficient E, and in number of molecules per cc. for the integrated intensity A; l, the thickness of the cell in cm.; ν, the frequency of the infrared rays in cycles per sec,; I_0 and I, the radiation intensity transmitted through the solvent and solution respectively.

Results

In the Table, the peak frequency (the band position) ν, the molar extinction coefficient E, the half-band width $\Delta\nu_{1/2}$, and the integrated intensity A are cited. Aniline and three isomers of toluidines, which are representatives of the compounds of the amino form, give rise to two absorption bands near 3480 cm.$^{-1}$ and 3390 cm.$^{-1}$, those bands having the intensities of the same order. The spectrum of 2-aminopyridine shows a similar tendency as the aforementioned four compounds. The heterocyclic compounds as pyrrole and indole, in which a hydrogen atom links to the ring nitrogen atom, show the spectra

TABLE I

OBSERVED VALUES OF THE N-H STRETCHING VIBRATIONS

Compounds	ν (cm.$^{-1}$)	$E\times10^{-4}$ (cm.^{2} mol.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	$A\times10^{8}$ (cm.^{2} molecule^{-1} sec.$^{-1}$)
Pyrrole	3495	25	13	65
Indole	3490	23	13	60
N-Methyl-2-pyridonimine	3322	1.8	24	9
2-Aminopyridine	3510 3410	5.4 7.6	32 25	28 31
Aniline	3481 3397	3.0 3.8	39 28	17 15
o-Toluidine*	3481 3399	3.1 3.5	35 26	15 12
m-Toluidine*	3479 3396	3.1 3.9	39 28	18 16
p-Toluidine*	3472 3391	2.9 3.6	39 29	17 16

* The data of toluidines are obtained with a calcium fluoride prism, whilst others with a lithium fluoride prism.

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[5] C. L. Angyal and R. L. Werner, ibid., 2911.

[6] J. D. S. Goulden, ibid., 2939.

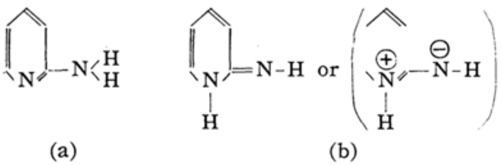
[7] The measurement was carried out in the Laboratory of Professor Kunio Kozima in Tokyo Institute of Technology, Tokyo.

[8] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

[9] This sample was kindly given by Mr. Takaaki Tamura, in this Institute.

with one sharp and intense absorption band attributed to the stretching vibration of the N-H link near 3490 cm.$^{-1}$. The spectrum of N-methyl-2-pyridonimine[10] which is selected as a representative of the compound of the imino form, shows a weak and broad band at 3322 cm^{-1}.

The above results are obtained from the measurements in a fairly dilute solution and there seems no absorption band which is ascribed to the associated molecule. From the data of the other authors[11] it can be also said that there will be no fear of the existence of the associated molecule in such a low concentration.



(a) (b)

Fig. 1. The tautomerism of 2-aminopyridine.

Discussion

As illustrated in the Table, the compounds of the amino form generally show two absorption bands with the same order of intensities near 3480 cm.$^{-1}$ and 3390cm^{-1}. Of these bands, the higher frequency one is assigned to the antisymmetric and the lower to the symmetric vibration of the NH_2 group, and the integrated intensity of the former is somewhat larger than the latter. While in 2-aminopyridine two bands are observed at 3510 cm.$^{-1}$ and 3410 cm.$^{-1}$ respectively and the integrated intensity of the former has larger value than the latter, the values of which are considerably larger than those of aniline etc. Although there are such trivial differences from aniline etc., the facts that the bands appear at the similar positions as aniline etc. and that intensities of the two bands have the values of the same order, show the coincidence of the spectrum of 2-aminopyridine with those of the compound of the amino form[12].

If 2-aminopyridine exists in the imino form, (Fig. 1b), then the absorption spectrum will show approximately the sum of the absorption assigned to the vibrations of the N-H link of pyrrole type and that of imino type; i.e., a sharp and strong band near 3490 cm.$^{-1}$ and a broad and extraordinarily weak band near 3320 cm^{-1}. This feature does not even qualitatively coincide with the observed spectrum of 2-aminopyridine. In fact, in the spectrum of 2-aminopyridine, there is no band near 3320 cm.$^{-1}$ and even if for some reasons this band would shift to about 3410 cm^{-1}., it will be impossible to explain the fact that the value of the integrated intensity of the band of the lower frequency vibration is apparently larger.

From those facts it will be concluded that 2-aminopyridine exists mainly or decidedly in the amino form in a dilute solution of the nonpolar solvent.

In the spectrum of 2-aminopyridine, a wing of the band of 3410 cm^{-1}. extends to 3320 cm^{-1}. but no superposition of bands is observed. If the tautomerism exists between the imino and the amino form (Fig. 1), considering the experimental accuracy and the noise level of spectrum, it is possible to estimate the ratio of the number of the molecules of imino structure allowed to exist to that of the amino structure. According to the simple calculation this possibility is estimated to be less than 0.5 %, hence even if there were a tautomerism it is concluded that the amino form is decidedly predominant over the imino form. This conclusion is consistent with the measurement on the pK_a, in which such a possibility is estimated to be less than 0.001 %[4].

Summary

The infrared absorption spectrum of 2-aminopyridine was observed and compared with those of other compounds and the amino form of 2-aminopyridine was confirmed. The imino form was rejected and even if this tautomeric form exists its quantity is estimated to be negligibly small.

The author wishes to express his hearty thanks to Assistant Professor Kenji Kuratani for his kind guidance and encouragement throughout this work. The author is indebted to Mr. Kiyoshi Sakashita in the Laboratory of Professor Kunio Kozima for his kind help at the time of the measurement of the infrared absorption spectra.

Institute of Science and Technology
University of Tokyo, Meguro-ku, Tokyo

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[10] N-Methyl-2-pyridonimine is very hygroscopic and even its dilute solution is not sufficiently transparent, but there is almost no influence of such a property on the observation.

[11] N. Fuson, M-L. Josien, R. L. Powell and E. Utterback, *J. Chem. Phys.*, **20**, 145 (1952).

[12] For the considerable increment of the intensity of 2-aminopyridine, the following qualitative explanation is given. Generally when the electrophilic radical or atom combines to the ring, the band shifts to the higher frequency[6] and the ionic character of NH bond is considered to increase, so that the change of the dipole moment in the vibration will become larger.