ON THE ELECTRONIC SPECTRA OF 2-AMINOPYRIDINE AND 3-AMINOPYRIDINE IN DIFFERENT STATES AND IN SOLUTIONS*

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Plate IX

ABSTRACT. The ultraviolet absorption spectra of 2-amino- and 3-aminopyridine in different states and also of their solutions in alcohol and n-hexane have been photographed and analysed. In the vapour phase, both the substances exhibit two systems of discrete bands due to $n \to \pi^*$ transition and $\pi \to \pi^*$ transition respectively. In the case of 2-aminopyridine in the liquid state and in solution, the system due to $\pi \to \pi^*$ transition shifts towards longer wavelengths so that the bands due to the $n \to \pi^*$ transition are not observed due to superposition of the two systems on each other. In the case of the solid state at the room temperature and also at -180°C, the spectrum seems to consist of two parts just separated from each other, the first part being the $\pi \to \pi^*$ system, which is shifted towards red by 3740 cm^{-1} and the second part is exactly in the same region in which the bands due to $n \to \pi^*$ transition in the vapour appear. In the case of 3-aminopyridine, the bands due to $n \to \pi^*$ transition is observed in the spectrum due to its solution in n-hexane, but no conclusion could be drawn regarding the presence or absence of $n \to \pi^*$ transition in the cases of solution in alcohol and pure liquid and also in the case of the solid at the room temperature and at -180°C owing to the superposition of the two systems.

It has been pointed out that the large shifts observed with the liquefaction of the vapour may be due to strong association of the molecules in the liquid state. There is also an increase in the width of the region of absorption with solidification of 3 aminopyridine and this has been attributed to the influence of neighbouring polar molecules in the crystal on the transition moment.

INTRODUCTION

It was first pointed out by Stephenson (1954) that near ultraviolet absorption spectrum of 3-bromopyridine in solution in iso-octane consists of two systems of bands due to $n \to \pi^*$ and $\pi \to \pi^*$ transitions, while in the case of 2-bromopyridine either in the solution or in the vapour state the former system is absent. It was also observed recently by the present author (Misra, 1960) that the spectrum of 3-bromopyridine in the vapour state consists of two systems of bands arising out

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of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions and in the spectrum of 2-bromopyridine in the vapour state the $n \rightarrow \pi^*$ transition is absent. As pointed out by Stephenson (1954), this is due to the inductive influence of the halogen atom on the sp^2 electron of the adjacent nitrogen atom. It was observed further (Misra, 1960) that in the case of 3-bromopyridine in the liquid state and in the solid state at -180 C, the $n \rightarrow \pi^*$ transition is absent and this was explained to be due to formation of associated groups through the non-bonding electron of the nitrogen atom and the hydrogen atom of the neighbouring molecules. The $n \rightarrow \pi^*$ transition was also found to be absent in the spectra due to solutions in alcohol because of formation of hydrogen bond through the sp^2 electron of the nitrogen atom of the pyridine ring and the OH group of the alcohol molecule. Similar conclusions were also drawn in the cases of pyridine and other substituted pyridines by Stephenson (1954), Banerjee (1956, 1957) and Roy (1958).

The ultraviolet absorption spectra of 2-amino and 3-aminopyridine in the vapour state did not appear to have been studied by any earlier worker and therefore, the influence of the NH_2 group on such $n \rightarrow \pi^*$ transition was not known. The present investigation was undertaken to analyse the absorption spectra of these two substances in the vapour state and also to study the influence of substitution of NH_2 group in place of the Br atom in the 2- and 3-position of the pyridine ring on the absorption spectra.

The absorption spectra of these two compounds in the liquid state, in the solid state at the room temperature and at -180 C and in solutions in different solvents have also been investigated in order to study the influence of different environments on the two transitions mentioned above.

E X P E R I M E N T A L

Chemically pure samples of 2-aminopyridine and 3-aminopyridine supplied by Fluka, Switzerland were fractionated and the proper fractions were distilled under reduced pressure just before use. Cells of length 50 cm, 25 cm and 10 cm were used to study the spectra due to the vapours. The absorption cell was filled up with the vapour at saturation vapour pressures at different temperatures. Two separate electrical heaters, one for the absorption cell and the other for the bulb containing the liquid and attached to the absorption cell, were used to control the temperature. The bulb containing the liquid was always kept at a temperature about 10°C lower than that at any part of the absorption cell.

To produce low pressures in the vapour in the absorption tube, the reservoir containing the liquid was immersed in suitable low temperature baths while the tube was left at the room temperature.

With an absorption cell of length 25 cm, the bulb containing the compound was kept at 35°C to record both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ system of 2-aminopyridine,

A 50 cm long absorption cell with the reservoir at 60°C was needed to record the bands due to the $n \to \pi^*$ and $\pi \to \pi^*$ transitions in 3-aminopyridine. The temperature of the bulb was raised to 70°C to record the $n \to \pi^*$ system distinctly.

Very thin films of thickness of the order of a few microns of the substances were required to produce the absorption bands in the solid state. To study the spectra in the liquid state, the thin films of the substances enclosed between two quartz plates were placed in a heating chamber which was kept at temperatures about 5°C above the respective melting points of the substances.

The solvents used to study the absorption spectra of the substances in the solutions were ethyl alcohol and n-hexane. The solvents were found to produce no absorption bands in the region under consideration. A brass cell of thickness 1 cm provided with quartz window was used for the solutions and the strength of the solution for each compound was about .01% by weight.

Spectrograms were taken on Agfa Isopan films backed by a metal sheet with a Hilger E 1 spectrograph giving a dispersion of the order of 3A per mm in the region of 2600Å. Iron arc spectrum was photographed on each spectrogram as a comparison.

Microphotometric records were taken with a Kipp and Zonen self-recording microphotometer. The absorption spectra were calibrated with the help of microphotometric records of the iron lines using the method described in an earlier paper (Sirkar and Misra, 1959). As the infrared absorption spectra of these substances had not been studied thoroughly by previous workers, the infrared absorption spectra of solution of 2-aminopyridine in CCl_4 and that of 3-aminipyridine in chloroform were recorded with a Perkin Elmer Model 21 spectrophotometer using rocksalt optics in order to find out the ground state vibrational frequencies and these were utilised to check the excited state frequencies obtained from the ultraviolet absorption spectra.

RESULTS AND DISCUSSIONS

2-Aminopyridine

Microphotometric records of the absorption spectra of 2-aminopyridine in different states and in solution in different solvents are reproduced in Figs. 1—3, and the spectrum of the substance in the vapour phase is reproduced in Plate IX, Fig. 4(a). The wave numbers of the bands in cm⁻¹ with their approximate strengths and probable assignments are given in Tables I-III.

(a) *Spectrum of the vapour phase* :

It can be seen from Fig. 1 that the absorption spectrum of 2-aminopyridine in the vapour phase shows two distinct systems of bands. One of these two systems (Transition I) consisting of sharp, narrow line-like bands starts from

about 32700 cm^{-1} and extends to the region of the other system which consists of broad bands resembling those due to other substituted benzenes. The former system has been attributed to the $n \rightarrow \pi^*$ transition after Kasha (1950) and the latter to the $\pi \rightarrow \pi^*$ transition. The analysis of the bands of these two systems is discussed separately in the following sections.

TABLE I

Ultraviolet absorption bands of 2-aminopyridine in the vapour phase

Transition I		Transition II	
wave number (cm^{-1}) and strength	Assignment	Wave number (cm^{-1}) and strength	Assignment
32885 (w)	0 — 564	34324 (s)	0,0
32999 (w)	0 — 455	34618 (w)	0 + 294
33070 (w)	0 — 379	34796 (s)	0 + 472
33157 (w)	0 — 292	34987 (m)	0 + 663
33223 (w)	0 — 226	35250 (s)	0 + 926
33364 (m)	0 + 210 — 292	35559 (s)	0 + 1235
33449 (vs)	0,0	35765 (s)	0 + 1441
33519 (w)	0 + 525 — 455	36025 (w)	0 + 1235 + 472
33660 (w)	0 + 210	36177 (ms)	0 + 2 × 926
33705 (m)	0 + 256	36572 (m)	0 + 2 × 663 + 926
33789 (s)	0 + 310	36896 (w)	0 + 2 × 663 + 1235
33879 (m)	0 + 430	37098 (m)	0 + 3 × 926
33974 (vs)	0 + 525		
34044 (m)	0 + 2 × 340 — 85		
34125 (w)	0 + 2 × 340 0 + 256 + 430		
34260 (w)	0 + 311		
34316 (w)	0 + 340 + 525 0 + 2 × 430		
34332 (w)	0 + 210 + 676		
34437 (vw)	0 + 988		
34496 (m)	0 + 2 × 525		
34857 (w)	0 + 1408 0 + 2 × 515 + 340		
34942 (w)	0 + 2 × 340 + 811		

(i)   *n → π* Transitions (Transition I)*

The sharp band at 33449 cm^{-1} which persists with undiminished intensity even at the low pressure of the absorbing vapour has been taken as the 0, 0 band of this system.   Most of the remaining strong bands represent transitions involving excited state vibration frequencies 210, 256, 340, 525, 811, 988 and 1408 cm^{-1} and also ground state frequencies 226, 292, 379, 455 and 564 cm^{-1} as shown in
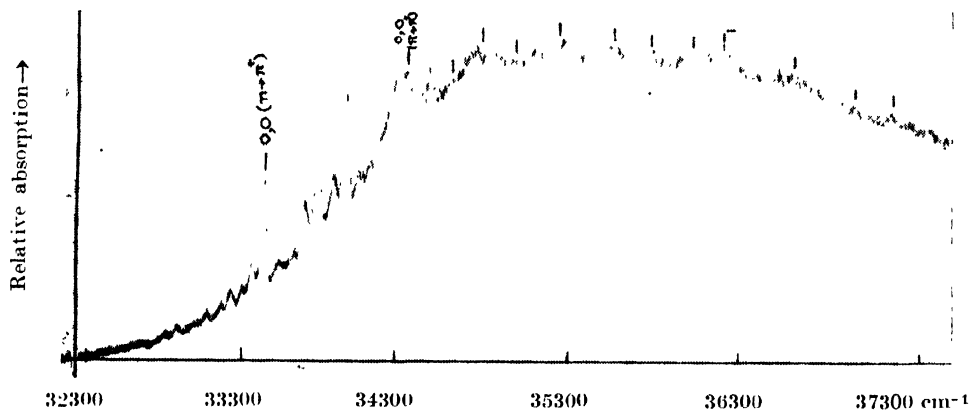

Fig. 1.   Microphotometric record of the ultraviolet absorption spectrum of 2-aminopyridine in the vapour phase.

Table 1.   The bands of wave numbers higher than 34125 cm^{-1} are superposed on those due to π→π* transition and this makes their accurate measurement somewhat uncertain.   The band of medium strength at 33364 cm^{-1} is probably not due to a v→0 transition as no corresponding 0→v transition with greater strength could be detected.   It was, therefore, assigned to a v→v' transition as shown in Table I.   The weak band at a distance of 70 cm^{-1} from the 0, 0 band on the high energy side is also similarly assigned as a v→v' transition.

(ii)   *π→π* Transition (Transition II)*

The band system in the region 34300 cm^{-1} to 37200 cm^{-1} consisting of broad bands which are distinctly different from the sharp narrow bands due to the Transition I has been attributed to the π→π* transition from their resemblance with the bands in the substituted benzene compounds.

It was difficult to find out the exact position of the 0, 0 band of this system because of the superposition of some bands due to n→π* transition on these bands. However, the centre of the strongest broad band on the long wavelength side of of this system is at 34324 cm^{-1} and this has been taken as the position of the 0, 0 band.   The other bands could then be assigned as progressions and combinations of excited state frequencies 294, 472, 663, 926, 1235 and 1441 cm^{-1}.

The infrared absorption spectrum above 990 cm^{-1} of this compound was earlier studied by Katritzky and Hands (1958) who reported the frequencies 991(ms)
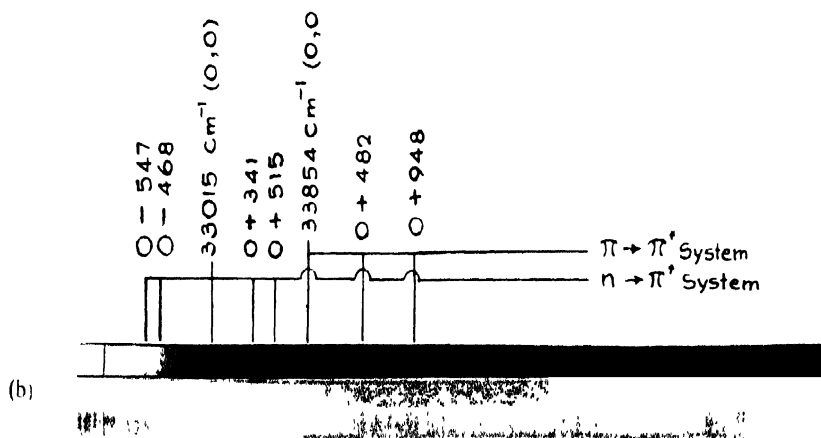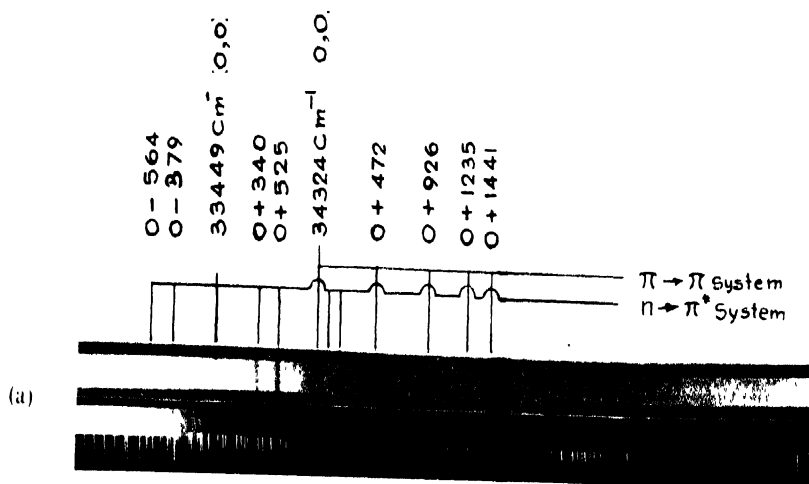
PLATE IX

Fig. 4. Ultraviolet absorption spectra of aminopyridines in the vapour phase

(a) 2- Aminopyridine vapour.

(b) 3- Aminopyridine vapour.

TABLE II

Ultraviolet absorption bands of 2-aminopyridine ($\pi \rightarrow \pi^*$ systems)

.01% solution in alcohol at 32°C		.01% solution in n-hexane at 32°C	
Wave number (cm⁻¹) and strength	Assignment	Wave number (cm⁻¹) and strength	Assignment
Broad absorption band extending from 32414 cm⁻¹ to 36000 cm⁻¹ without any discrete structure		32885 (s)	0,0
		33363 (m)	0 + 478
		33830 (m)	0 + 945
		34317 (m)	0 + 1432
		34782 (m)	0 + 2 × 945
		35755 (m)	0 + 2 × 1432

1038 (m), 1148 (s), 1270 (ms), 1317 (s), 1441 (s), 1483 (vs), 1574 (s) and 1602 (vs), being the strengths of the bands are given in parentheses. The infrared spectrum of solution of 2-aminopyridine in CCl_4 was reinvestigated down to 600 cm⁻¹ and besides the above frequencies a band at 710 cm⁻¹ was observed.

The excited state frequencies 663cm⁻¹, 926 cm⁻¹ and 1235 cm⁻¹ evidently correspond respectively to the ground state frequencies 710 cm⁻¹, 991 cm⁻¹ and 1270 cm⁻¹ observed in the infrared spectra. Two ground state frequencies 1441 cm⁻¹ and 1483 cm⁻¹ have been reported by Katritzky and Hands (1958) and it may be noted that the band assigned to the excited state frequency 1441 cm⁻¹ in the present investigation is quite broad and it may comprise two unresolved bands.

(b) *Influence of intermolecular field on the spectra*

    (i) *Spectra of the solutions*

In the spectrum of solution of 2-aminopyridine in n-hexane (Fig. 2) a band system consisting of broad absorption bands is observed in the region 32500 cm⁻¹
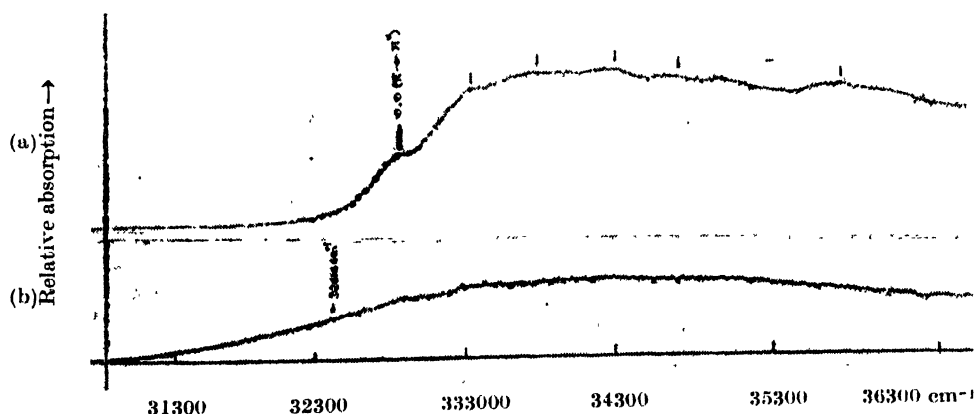

Fig. 2. Microphotometric records of the ultraviolet absorption spectra of solutions of 2-amino pyridine.

(a) .01% solution in n-hexane.   b) .01% solution in ethyl alcohol.

to 36000 cm⁻¹. From the structure of this band system, it appears that this system corresponds to the $\pi \to \pi^*$ transition in the vapour phase. Taking the first strong band at 32885 cm⁻¹ as the 0,0 band of this system, the other bands can be analysed in terms of the excited state frequencies 478 cm⁻¹, 945 cm⁻¹ and 1432 cm⁻¹ and their harmonics. Thus in the case of n-hexane solution this band system is shifted towards red by 1461 cm⁻¹. As the 0, 0 band in the $n \to \pi^*$ system due to the vapour is at 33449 cm⁻¹ and the 0, 0 band of the $\pi \to \pi^*$ transition in solution of hexane is at 32885 cm⁻¹ it is quite probable that the former system is masked by the strong system due to $\pi \to \pi^*$ transition.

In the spectrum of .01% solution of 2-aminopyridine in ethyl alcohol (Fig. 2) only one very broad band due to $\pi \to \pi^*$ transition is in the region 32000 cm⁻¹ to 36000 cm⁻¹. If the 0, 0 band is assumed to be at about 32414 cm⁻¹, which is the long wavelength edge of the borad band the band system seems to be shifted towards red by about 1910 cm⁻¹ from its position in the case of the vapour.

The appearance of the band system due to the solution in alcohol is different from that of the system due to the n-hexane solution and it is similar to that of the pure liquid. The shift of the system is also much larger than that observed in the case of the solution in hexane. These results probably indicate the formation of associated groups of 2-aminopyridine molecules with neighbouring alcohol molecules due to hydrogen bond-formation as suggested by Stephenson (1954) and Roy (1958) in the cases of other pyridine compounds.

(ii) *Spectra due to the substances in the liquid and solid states*

In the spectrum of 2-aminopyridine in the liquid state at 70°C a broad absorption band without any discrete structure is observed in the region from 32368
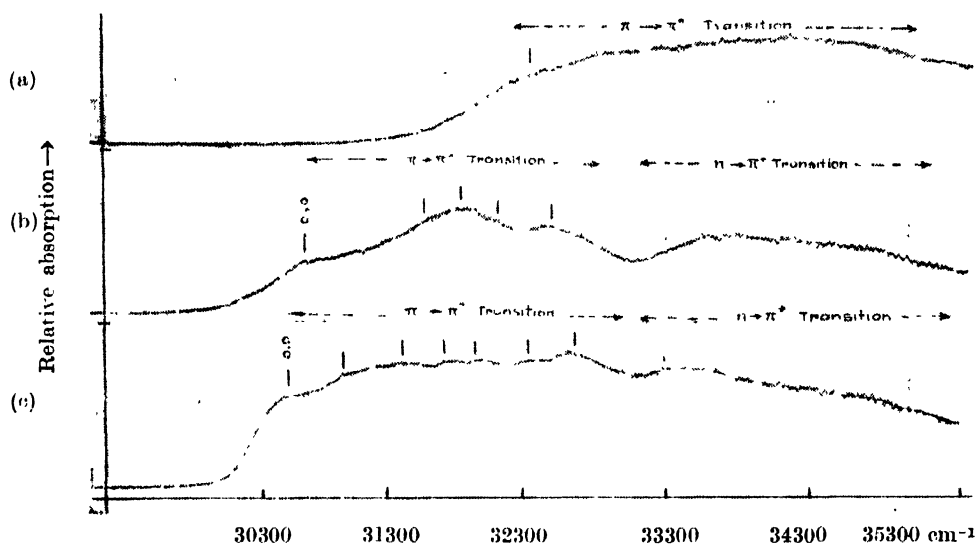

Fig. 3.   Microphotometric records of the ultraviolet absorption spectra of 2-aminopyridine.
(a)   Liquid at 70°C.   (b)   Solid at 33°C.   (c)   Solid at −180°C.

cm⁻¹ to 35421 cm⁻¹. This absroption appears to be due to the $\pi \to \pi^*$ transition. If we assume that the 0, 0 band of this transition lies near about the hump at 32368 cm⁻¹ on the long wavelength edge of the system, the 0, 0 band seems to be displaced towards red by about 2440 cm⁻¹ on liquefaction of the vapour.

This shift of the band system and the absence of discrete structure of the system may be due to formation of associated groups among neighbouring molecules. On comparing these results with those for the solution in alcohol it is found that the nature of association in the two cases is different, because the shift of the band system is much larger in the case of the pure liquid than in the solution in alcohol.

TABLE III

Ultraviolet absorption bands of 2-aminopyridine in the liquid and solid states

System	Liquid at 70 C		Solid at 32 C		Solid at 180°C	
	Wave number (cm⁻¹) and strength	Assignment	Wave number (cm⁻¹) and strength	Assignment	Wave number (cm⁻¹) and strength	Assignment
Transition II	Broad absorption extending from 32368 cm⁻¹ to 35421 cm⁻¹		30684 (m) 31611 (m) 31929 (s) 32134 (m) 32535 (m)	0,0 0 927 0 1245 0 1450 0 2 927	30497 (s) 30968 (m) 31430 (m) 31716 (m) 31964 (m) 31357 (m) 32680 (ms)	0,0 0 471 0 933 0 1249 0 1467 0 2×93 0 933+ 1249
tion I	Not observed		Board band in the region 33300 cm⁻¹ —35000 cm⁻¹		Board band in the region 33300 cm⁻¹ —35000 cm⁻¹	

When the liquid is solidified at room temperature discrete band structure is observed, but the spectrum seems to be somewhat different from that due to the vapour phase. Not only the band system due to the solid is shifted towards red but also the individual bands are much broader so that they are not resolved clearly. This may be due to small splitting caused by the influence of the neighbouring polar molecules in the crystal on the transition moment. Taking the 0, 0 band to be at 30684 cm⁻¹ the excited state frequencies 927 cm⁻¹, 1245 cm⁻¹ and 1450 cm⁻¹ may be attributed to the other bands. It also appears that the spectrum consists of two parts, the second part starting from about 33200 cm⁻¹ and extending upto about 35000 cm⁻¹. As the 0, 0 band of the $n \to \pi^*$ system of the vapour is at 33449 cm⁻¹ probably this second portion of the spectrum due to the substance in the solid state is produced by the $n \to \pi^*$ transition. The bands due to $n \to \pi^*$ transition are too broad to be resolved from each other probably

because of the same reason as indicated above. Thus it appears that in this case the $n \to \pi^*$ transition persists in the solid state. In the spectrum due to the liquid also, this second part seems to be superposed on the first part but the shift of the first part being smaller than that in the case of the solid the two parts are not separated from each other.

When the solid is cooled to $-180^\circ C$, the bands are found to remain broad and the absorption becomes stronger. The strong band at 30497 cm^{-1} has been taken as the 0,0 band and the upper state fundamentals 471, 933, 1249 and 1467 cm^{-1} have been observed, as shown in Table III. The second part due to $n \to \pi^*$ transition seems to persist at $-180^\circ C$ in the same position as at the room temperature.

As the $n \to \pi^*$ transition seems to persist in this solid state also, it seems that the nitrogen atom of the ring does not take part in weak bond-formation. It is quite probable that the NH_2 group is responsible for hydrogen bond-formation with the neighbouring molecules and in that case the effect is expected to be similar to that of the substitution of a hydrogen atom of the ring and consequently a shift of the band system towards red is expected. In the case of the solid at the room temperature the shift is about 3740 cm^{-1} from its position in the case of the vapour, while with further cooling to $-180^\circ C$, the 0, 0 band experiences a further shift of 187 cm^{-1} towards red. The large shift of the 0, 0 band on solidification of the liquid and very small shift with further cooling and also the small splitting to which the broadening of the bands were attributed may be due to the influence of intermolecular field in the crystal on the electronic energy levels of the molecule.

3-Aminopyridine

Microphotometric records of the absorption spectra of 3-aminopyridine in different states and in solutions in different solvents are reproduced in Figs. 5-7 and the spectrum of the substance in the vapour phase is reproduced in Plate IX, Fig. 4(b). Wave numbers of the bands in cm^{-1}, their approximate strengths and their probable assignments are given in Table IV-VI.

(a) *Spectrum due to the vapour phase*

The absorption spectrum of 3-aminopyridine in the vapour phase shows two distinct systems of bands as shown in Fig. 5. In the case of the vapour at the saturation pressure at $60^\circ C$ and with a path length of 50 cm a system consisting of sharp, narrow bands appears on the long wavelength side of another system consisting of broad bands. As in the case of 2-aminopyridine, the former system has been attributed to the $n \to \pi^*$ transition and the latter to the $\pi \to \pi^*$ transition.
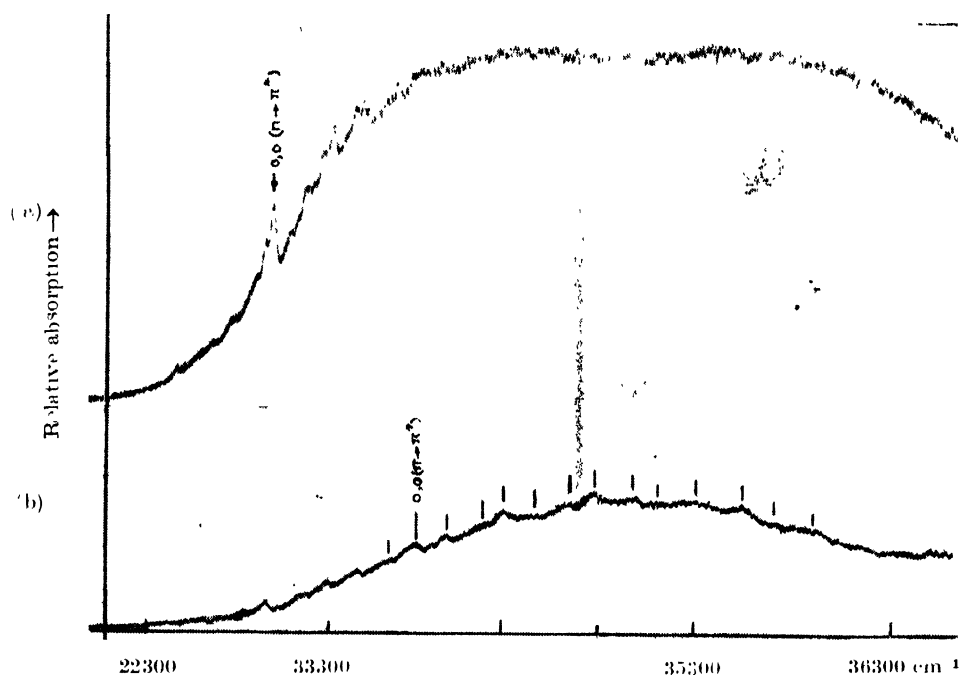
Fig. 5. Microphotometric records of the ultraviolet absorption speectra of 3-aminopyridine in the vapour phase.
(a) $n \rightarrow \pi^*$ transition. (b) $\pi \rightarrow \pi^*$ transition.

TABLE IV

Ultraviolet absorption bands of 3-aminopyridine in the vapour phase

Transition I		Transition II	
Wave number (cm⁻¹) and strength	Assignment	Wave number (cm⁻¹) and strength	Assignment
32462 (w)	0 — 547	33690 (m)	0 — 164
32547 (w)	0 — 468	33854 (s)	0,0
32691 (w)	0 — 324	34004 (ms)	0 + 150
32777 (m)	0 — 238	34208 (m)	0 + 354
32891 (w)	0 — 124	34336 (s)	0 + 482
32961 (w)	0 + 181 — 238	34494 (w)	0 + 640
33015 (vs)	0,0	34712 (m)	0 + 858
33119 (m)	0 + 104	34802 (s)	0 + 948
33196 (m)	0 + 181	35009 (m)	0 + 1160 / 0 + 2 × 150 + 858
33301 (m)	0 + 270	35128 (m)	0 + 1274 / 0 + 2 × 640
33356 (s)	0 + 341	35353 (m)	0 + 1499 / 0 + 858 + 640
33520 (m)	0 + 515	35579 (w)	0 + 2 × 858
		35754 (w)	0 + 2 × 948
		35918 (w)	0 + 150 + 2 × 948

(i) $n \rightarrow \pi^*$ transition   (Transition I)

The bands due to $n \rightarrow \pi^*$ transition in 3-aminopyridine lie in the region 32300 cm^{-1} to 33800 cm^{-1}. The sharp and strong band at 33015 cm^{-1} has been taken as the 0, 0 band of the system the other bands have been analysed in terms of upper state fundamentals 104, 181, 270, 341 and 515 cm^{-1} and their combinations. The corresponding ground state vibrational wave numbers as obtained from $v \rightarrow 0$ transitions are probably 124, 238, 324, 468 and 547 cm^{-1}.

It may be noted for comparison that the excited state variational wave numbers 131 cm^{-1}, 158 cm^{-1}, 264 cm^{-1} 499 cm^{-1}, 545 cm^{-1} and 580 cm^{-1} were reported by Rush and Sponer (1952) in the case of $n \rightarrow \pi^*$ transition in 3-methyl pyridine and in the case of 3-bromopyridine the corresponding wave numbers were found to be 230 cm^{-1}, 279 cm^{-1}, 349 cm^{-1} and 579 cm^{-1} (Misra, 1960).

The band at 32961 cm^{-1} on the longer wavelength side of the 0, 0 band has been assigned as a $v \rightarrow v'$ transition. The assignments of the bands on the high energy side of the system is somewhat uncertain due to overlapping of the bands due to $n \rightarrow \pi^*$ transition with those due to $\pi \rightarrow \pi^*$ transition.

(ii) $\pi \rightarrow \pi^*$ transitions   (Transition II)

The band system due to $\pi \rightarrow \pi^*$ transition in 3-aminopyridine in the vapour phase lies in the region from 33600 cm^{-1} to 36500 cm^{-1}. As in the case of 2-amino-pyridine there is some uncertainty in locating exactly the 0, 0 band of this system due to the overlapping of the two transitions in this region, as stated in the previous section. However, the strong band on the long wavelength side of this system at 33854 cm^{-1} whereform the broad absorption system seems to start at higher pressure of the absorbing vapour is taken tentatively as the 0, 0 band. Most of the remaining bands represent transitions involving excited state vibrational frequencies 150, 354, 482, 640, 858, 948, 1160, 1274 and 1499 cm^{-1} as shown in Table IV. Moreover, a ground state frequency 164 cm^{-1} is observed as $v \rightarrow 0$ transition. In order to find out the ground state vibrational frequencies, the infrared absorption spectrum of 3-aminopyridine in chloroform solution was studied with a Perkin Elmer Model 21 spectrophotometer with NaCl optics. The wave numbers of some of the observed infrared bands are 690 (m), 790 (m), 885 (m), 1013(s), 1042(s), 1090 (w), 1220 (w), 1255 (m), 1285 (s), 1438 (vs), 1485 (s), 1580 (vs) cm^{-1}, the strength of absorption being given in the paretheses. The infrared frequencies 690 cm^{-1} and 885 cm^{-1} may correspond to the excited state frequencies 640 cm^{-1} and 858 cm^{-1} observed in the ultraviolet absorption spectrum. There are two medium strong infrared absorption bands of ground state frequencies 1013 cm^{-1} and 1042 cm^{-1} but only one excited state frequency 948 cm^{-1} is observed in the ultraviolet absorption spectrum. The bands at a distance of 1160 cm^{-1}, 1274 cm^{-1} and 1499 cm^{-1} from the 0, 0 band shown as combinations, may also be fundamentals as there are strong bands with vibrational frequencies 1220 cm^{-1}, 1285 cm^{-1} and 1580 cm^{-1} in the infrared spectrum.

(b) *Influence of intermolecular field on the spectra*

(i) *Spectra due to the solutions*

In the spectrum of 3-aminopyridine in *n*-hexane solution broad absorption bands corresponding to those due to the $\pi \rightarrow \pi^*$ transition in the vapour phase
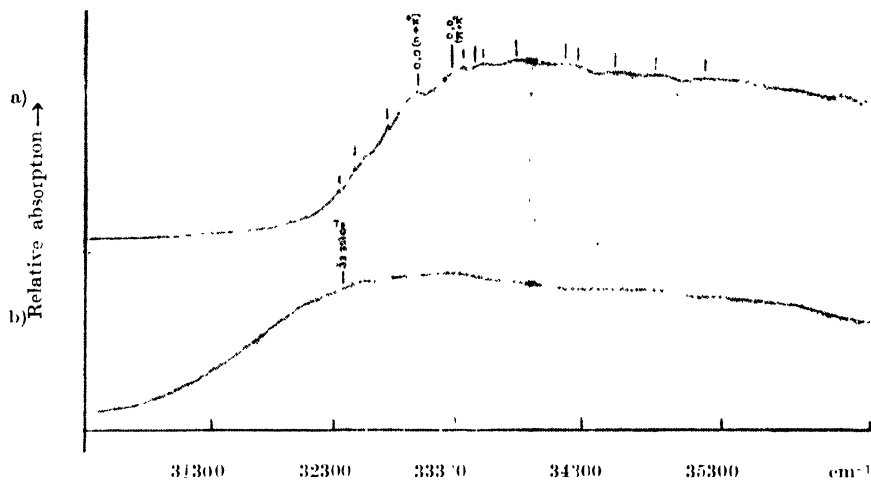

Fig. 6. Microphotometric record of the ultraviolet absorption spectra of solutions of 3-aminopyridine.

(a) .01% solution in *n*-hexane.   (b) .01% solution in ethyl alcohol.

TABLE V

Ultraviolet absorption bands of 3-aminopyridine in solution

System	Solution in alcohol at 32°C		Solution in *n*-hexane at 32°C	
	Wave number (cm⁻¹) and strength	Assignment	Wave number (cm⁻¹) and strength	Assignment
Transition II	Broad absorption band extending from 31437 cm⁻¹ to 35857 cm⁻¹		33301 (s)	0,0
			33461 (m)	0 + 160
			33779 (m)	0 + 478
			34154 (m)	0 + 853
			34248 (m)	0 + 947
			34473 (m)	0 + 1173
			34784 (m)	0 + 1483
			35200 (m)	0 + 2 × 947
Transition I	Absent		32472 (w)	0 — 543
			32776 (w)	0 — 239
			33015 (s)	0,0
			33357 (w)	0 + 342
			33524 (m)	0) + 509

are observed. Assuming the broad band at 33301 cm^{-1} as the 0, 0 band of the system, the other bands can be explained in terms of excited state frequencies 160, 478, 853, 947, 1173, 1483 cm^{-1} and their combinations as shown in Table V. These upper state fundamentals agree fairly well with those observed in the spectrum due to the vapour.

In addition to the above broad bands a few sharp weak bands are also observed in the spectrum of 3-aminopyridine in *n*-hexane solution at 33015, 32776 and 32468 cm^{-1}. There are also two weak bands at 33357 cm^{-1} and 33520 cm^{-1}. The positions of these bands are found to be indentical with those of bands of $n{\rightarrow}\pi^*$ system due to the vapour phase and therefore the $n{\rightarrow}\pi^*$ system persists in the solution in *n*-hexane. So, the $n{\rightarrow}\pi^*$ transition is not affected appreciably by the solvent molecules.

In alcohol solution, however, no banded structure is observed and only a very broad absorption band extending from 31437 cm^{-1} to 35857 cm^{-1} is observed. As in the case of 2-amino isomer, this absorption seems to correspond to the $\pi{\rightarrow}\pi^*$ transition. The absorption increases rapidly and becomes large at 32321 cm^{-1}. So, the system seems to be shifted by about 1500 cm^{-1} towards red from its position in the spectrum due to the vapour. The position of the system due to the $n{\rightarrow}\pi^*$ transition is almost at the maximum of the broad band. So it is not possible to come to any conclusion regarding the appearance or otherwise of this system in case of the solution in alcohol.
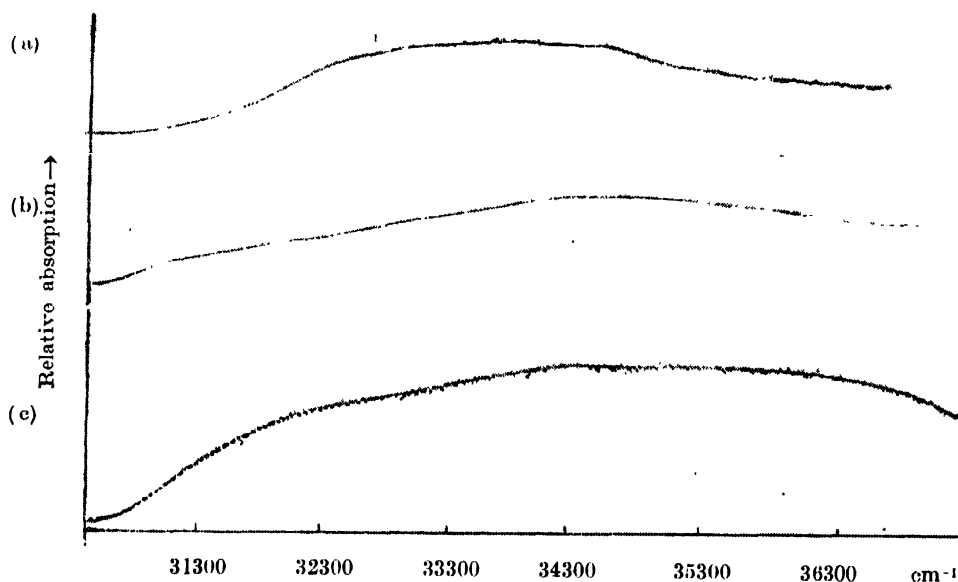

Fig. 7. Microphotometric records of the ultraviolet absorption spectra of 3-aminopyridine

(a) Liquid at 70°C.   (b) Solid at 32°C.   (c) Solid at −180°C.

(ii) *Spectra in the liquid and solid states*

In the liquid state 3-aminopyridine shows only a very broad absorption band without any discrete structure in the region 31650 cm^{-1} to 35450 cm^{-1} as shown in Fig. 7. The appearance is similar to that due to the solution in alcohol. In this case also nothing can be said about the presence or absence of the system due to the $n \rightarrow \pi^*$ transition.

TABLE VI

Ultraviolet absorption bands of 3-aminopyridine in the liquid and solid states

Liquid at 70°C	Solid at 32°C	Solid at −180°C
Broad absorption band extending from 31650 cm^{-1} to 35450 cm^{-1}	Broad absorption band extending from 30760 cm^{-1} to 36780 cm^{-1}	Broad absorption band extending from 30760 cm^{-1} to 36780 cm^{-1}

When the substance is solidified at the room temperature no discrete structure of the band system is observed but the region of absorption becomes extended on both sides. When the substance is further cooled to −180°C, no further appreciable change in the spectrum takes place. It is interesting, however, that in this case the width of the region of absorption is about 6000 cm^{-1}. This is double the breadth of the $\pi \rightarrow \pi^*$ system due to the vapour phase. This increase in the width of the region may be due to the large unresolved splitting of the system caused by the intermolecular field in the crystal lattice.

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