On the electronic spectra of 2, 5-and 2, 6-dibromopyridines

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The near ultraviolet absorption spectra of 2,5- and 2,6-dibromo-pyridine in the vapour state and in solutions in cyclohexane and ethyl alcohol have been studied and their vibrational structures have been analysed. Both compounds exhibit only one system of bands due to $\pi \rightarrow \pi^*$ transition in the vapour state and in solutions Solvent shifts of the 0,0 bands in solutions in the two solvents have been discussed

INTRODUCTION

The appearance of two systems of bands due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the absorption spectra of pyridine and substituted pyridines and the effect of solvents on the two systems were discussed by Kasha (1950) and Brealey & Kasha (1955). Solution and vapour spectra of several mono- and di-substituted pyridines have been described by different authors (Herrington 1950, Rush & Sponer 1952, Andon *et al* 1954, Ikekawa & Sato 1956, Kyte *et al*. 1960, Pandey 1967, and Bag 1971). Stephenson (1954) studied the solution spectra of 2- and 3-bromopyridine and observed that 3-bromopyridine yields both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ systems of absorption bands while the spectrum of 2-bromopyridine exhibits only the $\pi \rightarrow \pi^*$ system of bands. These observations were later corroborated by Misra (1960)

The ultraviolet absorption spectrum of 2,5-dibromopyridine was reported by Spiers & Wibaut (1937) without any analysis. The spectrum of 2,6-dibromopyridine has not been reported by any author. In the present work, the absorption spectra of 2,5- and 2,6-dibromopyridine in the vapour state and in solutions in cyclohexane and ethyl alcohol have been photographed and analysed Since data on the ground state vibrational frequencies of the two molecules are not available in the literature their infrared absorption spectra have also been recorded.

EXPERIMENTAL

Pure samples of 2,5- and 2,6-dibromopyridine were obtained from Schuckardt, München (Germany). The samples were fractionated and the proper fraction of each sample was further distilled under reduced pressure before being used.

The experimental arrangements for studying the electronic spectra were similar to those described in an earlier paper (Marjit 1970). The spectra were photographed on Kodak Spectrum Analysis Film No 1 with an all metal Hilger El (E478) quartz spectrograph having an inverse dispersion of about 3 Å/mm in the 2600 Å region. Iron arc comparison spectrum was photographed on each spectrogram by means of Hartmann's diaphragm.

Microphotometric records of the spectra were taken with a Kipp and Zonen Moll microphotometer. The accuracy in the measurements of the positions of absorption bands was about ± 10 cm^{-1} for sharp and moderately sharp bands.

The infrared absorption spectra of the compounds in dry ether in the 600–2000 cm^{-1} region were recorded with a Perkin Elmer model 21 double beam spectrophotometer equipped with rock salt optics

RESULTS

The microphotometric records of the absorption spectra of 2,5- and 2,6-dibromopyridine in the vapour state and in solutions are reproduced in figures 1–4. The wave numbers of the absorption bands with probable assignments are given in tables 1–6. The infrared frequencies are given in table 7.
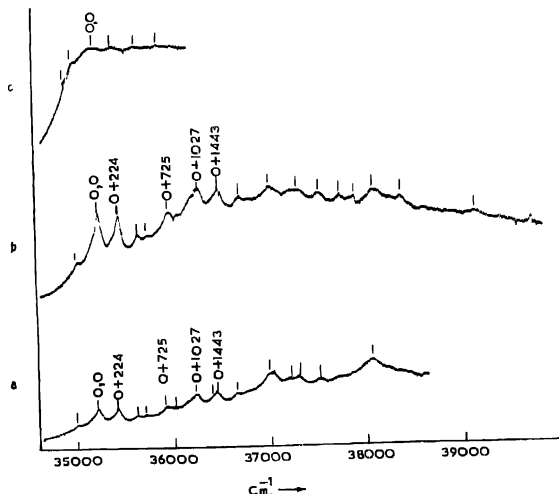

Figure 1. Microphotometric records of the ultraviolet absorption spectra in Transition II ($\pi \rightarrow \pi^*$) of 2,5-dibromopyridine in the vapour state. (a) 30 cm cell at 70°C. (b) 100 cm cell at 40°C (c) 100 cm cell at 120°C.
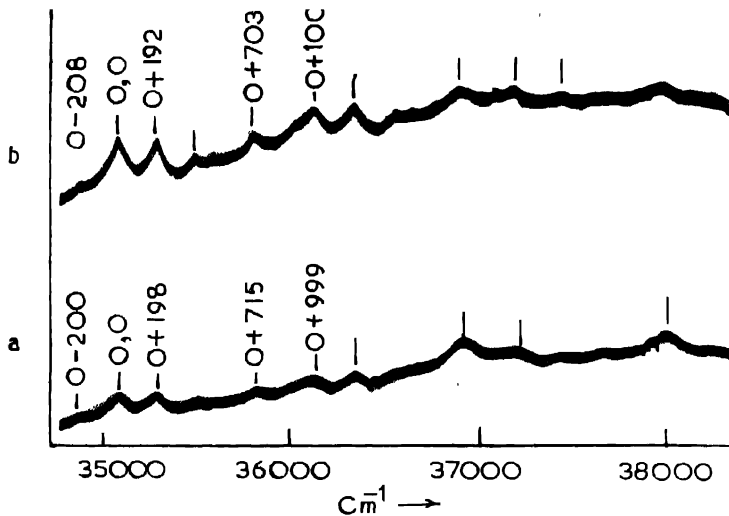
Figure 2   Microphotometric records of the ultraviolet absorption spectra of:
(a) $8.5 \times 10^{-4}M$ solution of 2,5-dibromopyridine in ethyl alcohol at 32°C
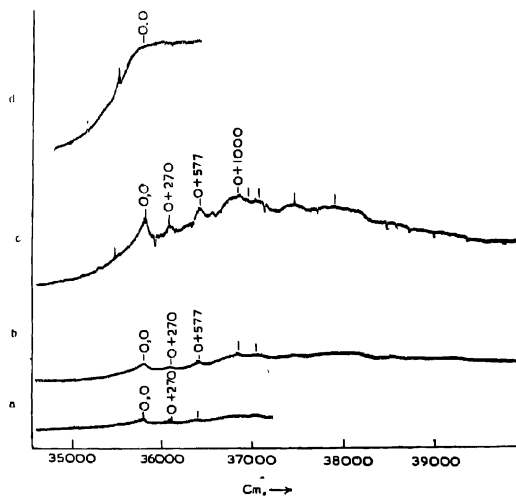(b) $9.5 \times 10^{-4}M$ solution of 2,5-dibromopyridine in cyclohexane at 32°C

Figure 3.   Microphotometric records of the ultraviolet absorption spectra in Transition II $(\pi \rightarrow \pi^*)$ of 2,6-dibromopyridine in the vapour state. (a) 30 cm cell at 0°C (b) 30 cm cell at 70°C. (c) 100 cm cell at 48°C. (d) 100 cm cell at 140°C.
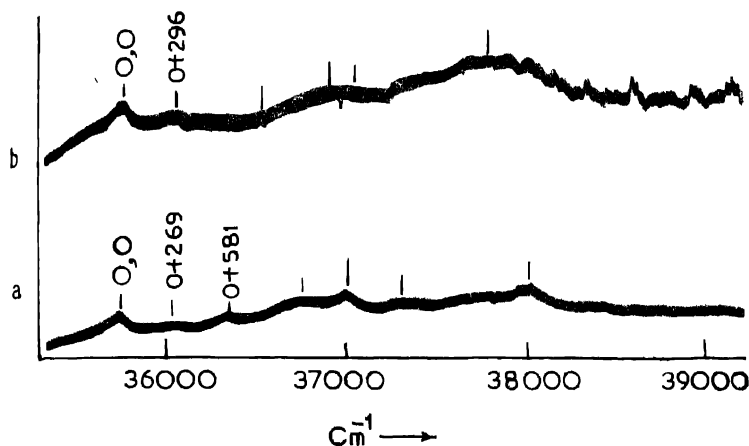
Figure 4   Microphotometric records of the ultraviolet absorption spectra of :
   (a) $8.5 \times 10^{-4} M$ solution of 2,6-dibromopyridine in ethyl alcohol at 35°C
   (b) $9.3 \times 10^{-4} M$ solution of 2,6-dibromopyridine in cyclohexane at 35°C.

DISCUSSION

Under widely different conditions of temperature and pressure and lengths of the absorbing vapour column the spectra of both 2,5- and 2,6-dibromopyridines in the vapour state appear to consist of only one strong system of absorption bands in the 2500–2900 Å region   The absorption spectra of the solutions of the two compounds in both cyclohexane and ethyl alcohol more or less retain the vibrational structure observed in the corresponding vapour spectrum.   In the case of solution in cyclohexane the band system due to each molecule undergoes a small red shift with respect to that of the corresponding vapour.   On changing the solvent to proton donor ethyl alcohol, the 0,0 band shows a similar red shift.   Since the $\pi \to \pi^*$ system always undergo bathochromic shifts irrespective of the nature of the solvent, the above facts probably indicate that the band system may be due to $\pi \to \pi^*$ transition in both the molecules.   The existence of a second system of bands attributable to $n \to \pi^*$ transition could not be detected in the vapour spectra or the solution spectra of the two compounds. This observation is similar to that reported by Stephenson (1954) for the 2-bromopyridine molecule.

Table 1. Ultraviolet absorption bands at 2,5-dibromopyridine in the vapour state ($\pi \to \pi^*$ transition)

Wave No (cm⁻¹)	Intensity					Difference from the 0,0 band	Assignment
	$L^* = 100$ cm		$L = 30$ cm				
	$t = 40°C$	$t = 120°C$	$t = 0°C$	$t = 30°C$	$t - 70°C$		
34837	w	mw		m	w	− 302	0−302
34918	m	ms		m	m	− 221	0−221
35074	ms	s			m	− 55	0−221+149
35139	vs	vs	w	m	s	0	0,0
35288	w	−			vw	+ 149	0 + 149
35363	vs	s	w	m	s	+ 224	0+224
35556	m				m	+ 417	0+417
35659	m	↓			m	+ 520	0+520
35793	m				mw	+ 654	0+654
35864	s	cut off			s	+ 725	0+725
35943	m				m	+ 804	0+804
36038	m				mw	+ 899	0+899
36077	ms				m	+ 938	0+938
36166	vs				s	+1027	0+1027
36287	m				mw	+1148	0+1148; 0+417+725
36392	vs				s	+1253	0+1253; 0+520+725
36579	m				mw	+1440	0+1440; 0+2×725 ⎱ 0+417+1027 ⎰
36651	ms				m	+1522	0+1522, 0+725+804
36673	w				w	+1534	0+520+1027
36750	w				w	+1611	0+2×804, 0+725+899
36903						+1764	0+725+1027 ⎱ 0+520+1253 ⎰
37081						+1943	0+938+1027
37178						+2039	0+2×1027
37414						+2275	0+1027+1253
37597						+2458	0+2×1027+654 ⎱ 0+1027+1440 ⎰
37812						+2673	0+2×1027+654
38406						+3267	0+2×1027+1253
38869						+3730	0+3×1027+725

L^* = Length of the absorption tube.

Table 2   Ultraviolet absorption bands of 2,5-dibromopyride in solutions

$$(\pi \rightarrow \pi^* \text{ transition})$$

Solution in cyclohexane ($9{\cdot}3 \times 10^{-4}M$ at 35°C)			Solution in ethyl alcohol ($8.5 \times 10^{-4}M$ at 35°C)		
Wave No. in cm⁻¹ & Intensity	Difference from the 0,0 band	Assignment	Wave No in cm⁻¹ & Intensity	Difference from the 0,0 band	Assignment
34882 w	− 208	0 − 208	34865 w	− 200	0 −200
35090 s	0	0,0	35065 s	0	0,0
35295 s	+ 205	0+205	35263 s	+ 198	0+198
35803 ms	+ 713	0+713	35780 m	+ 715	0+715
36035 ms	+ 945	0+945	36024 m	+ 959	0+959
36113 ms	+1023	0+1023	36096 ms	+1031	0+1031
36250 m	+1160	0+1160	36493 ms	+1428	0+1428 ⎫ 0+2×715 ⎬
36505 ms	+1415	0+1415 ⎫ 0+2×713 ⎬	36822 vs	+1757	0+1031+715
36825 vs	+1735	0+1023+713	37122 m	+2057	0+2×1031
37136 m	+2046	0+2×1023	37825 ms	+2760	0+2×1031+715
37850 s	+2760	0+2×1023+713			

Table 3   Probable correlation between the ground state and excited state fundamentals of 2,5-dibromopyridine

Gound state fundamentals (cm⁻¹)		Excited state fundamentals	Probable nature of mode
Infrared absorption	Ultraviolet absorption (Vapour state)	Ultraviolet absorption (cm⁻¹) (Vapour state)	
.	—	149	
---	221	224	
—	302	—	
—	—	417	ϕ (CC)
—	—	520	ϕ (CCC)
680	—	654	
750	—	725	
828	—	804	
918	—	899	
990	—	938	
1090	—	1027	β (CN)
1170	—	1148	β (CH)
1310	—	1253	γ (CC, CN)
1491	—	1440	

Table 4. Ultraviolet absorption bands of 2,6-dibromopyridine in the vapour state ($\pi \to \pi^*$ transition)

Wave No. (cm⁻¹)	Intensity					Difference from the 0,0 band	Assignment
	$L^* = 100$ cm		$L = 30$ cm				
	$t = 40°C$	$t = 120°C$	$t = 0°C$	$t = 30°C$	$t = 70°C$		
35425	w	mw	vw	vw	vw	− 285	0−285
35545	w	mw	vw	vw	vw	− 165	0−165
35710	vs	s	w	w	s	0	0,0
35870	w		—	—	w	+ 160	0+160
35980	ms	↓			m	+ 270	0+270
36181	m				mw	+ 471	0+471
36287	s				ms	+ 577	0+577
36592	ms	cut			m	+ 882	0+882
36619	m	off			mw	+ 909	0+909
36713	s				ms	+1003	0+1003
36794	m				m	+1084	0+1084
36889	ms				m	+1179	0+270+909
36937	m				m	+1227	0+1227
37191	m				m	+1481	0+577+909 0+471+1003
37281	m				mw	+1578	0+577+1003
37625	m				mw	+1915	0+909+1003
37708	mw				mw	+1998	0+2×1003
37868	m				m	+2158	0+2×1084
38279	w				mw	+2569	0+2×1003+577

$L^* =$ length of the absorption tube

Table 5. Ultraviolet absorption bands of 2,6-dibromopyridine in solutions ($\pi \to \pi^*$ transition)

Solution in cyclohexane (9.3×10⁻⁵M at 35°C)			Solution in ethyl alcohol (8.5×10⁻⁴M at 35°C)		
Wave No. in cm⁻¹ & Intensity	Difference from the 0,0 band	Assignment	Wave No. in cm⁻¹ & Intensity	Difference from the 0,0 band	Assignment
35652 s	0	0,0	35627 s	0	0,0
35948 m	+ 296	0+296	35896 m	+ 269	0+269
36234 ms	+ 582	0+582	36208 ms	+ 581	0+581
36652 m	+1000	0+1000	36586 m	+ 959	0+959
36905 s	+1253	0+1253	36822 s	+1195	0+959+269
37224 m	+1572	0+1000+582	37166 m	+1539	0+959+581
37825 s	+2173	—			

Table 6. Probable correlation between the ground state and excited state fundamental of 2,6-dibromopyridine

Ground state fundamentals		Excited state fundamentals	Probable nature of mode
Infrared absorption	Ultraviolet absorption (Vapour state)	Ultraviolet absorption (Vapour state)	
—	165	160	
—	285	270	
—	—	471	
—	—	577	α (CCC)
914	—	822	
930	—	909	
1018	—	1003	Ring
1094	—	1084	β (CH)
1276	—	1227	γ (CC, CN)

Table 7. Infrared frequencies of dibromopyridines in cm^{-1}
(3% solution in dry ether)

2,5-dibromopyridine	2,6-dibromopyridine	2,5-dibromopyridine	2,6-dibromopyridine
601 vvw	—	—	1144 m
610 w	—	1170 s	1173 m
—	638 ms	1200 ms	—
680 m	—	—	1217 w
710 m	710 m	1240 m	—
—	725 m	1250 w	1276 m
750 m	740 vs	1310 s	1288 ms
760 w	—	1320 s	—
768 w	—	1330 m	—
780 m	780 s	1342 w	1346 s
796 s	—	—	1376 vs
810 m	812 s	—	1401 vs
828 m	825 s	—	1408 s
860 ms	840 vs	—	1438 vs
880 ms	881 m	1470 w	—
898 w	—	1491 m	1484 ms
918 w	914 s	1510 w	—
940 ms	930 s	1527 s	1521 w
990 ms	984 s	1540 s	1540 vs
1004 vs	1018 s	1580 m	—
—	1036 s	1600 m	—
1080 s	1074 s	1613 w	—
1090 vs	1094 vs	1805 vvw	—
—	1112 s	1952 vvw	—

2,5-dibromopyridine

In the vapour state 2,5-dibromopyridine yields about twenty eight sharp absorption bands. From a study of the temperature dependence of the intensities of the bands the 0,0 band of the system has been taken at 35139 cm^{-1}. The bands to the shorter wave length side of the band origin in the vapour spectra have been analyzed in terms of the excited state fundamentals 149, 224, 417, 520, 654, 725, 804, 938, 1027, 1148, 1253 and 1440 cm^{-1}. The most prominent frequency appearing in progression or in combination with other frequencies is 1027 cm^{-1}. Probable correlation of some of the excited state frequencies with the ground state infrared frequencies is given in table 3.

The frequencies 221 and 302 cm^{-1} observed on the long wave length side of the 0,0 band in the ultraviolet absorption spectrum of the vapour probably represent ground state fundamentals.

In the absorption spectra of solutions of 2,5-dibromopyridine in cyclohexane and ethyl alcohol the strongest bands on the long wave length side at 35090 cm^{-1} and 35065 cm^{-1}, respectively, have been taken as 0,0 band. Thus in either solvent the 0,0 band undergoes a small red shift with respect to the 0,0 band of the vapour which is characteristic of the $\pi \to \pi^*$ transition.

2,6-dibromopyridine

The spectrum of 2,6-dibromopyridine in the vapour state shows about twenty absorption bands in the region 35000–38500 cm^{-1}. The band at 35710 cm^{-1} which persists with relatively undiminished intensity at low pressures of the absorbing vapour has been taken as the 0,0 band of the system. The other bands are found to involve excited state fundamentals 160, 270, 471, 551, 882, 909, 1003, 1084 and 1227 cm^{-1} and two gound state fundamentals 165 and 285 cm^{-1}. Probable correlation of some of the excited state frequencies with the ground state infrared frequencies is shown in table 6.

In the absorption spectra of solutions of 2,6-dibromopyridine in cyclohexane and ethyl alcohol, the 0,0 bands have been assigned to the strongest bands at 35652 cm^{-1} and 335627 cm^{-1} respectively. In this case also the 0,0 band undergoes a small red shift characteristic of the $\pi \to \pi^*$ transition.

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