

## Electronic absorption spectrum of 5-methylpyrimidine

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The ultraviolet absorption spectrum of 5-methylpyrimidine in the vapour state and in solution have been studied. Two electronic band systems due to  $n-\pi^*$  and  $\pi-\pi^*$  transitions have been observed. The observed fundamentals and their assignments are reported and discussed.

### 1. INTRODUCTION

The electronic absorption spectrum of pyrimidine has been studied in great detail by different authors (Uber 1941, Limes *et al* 1967, 1969). In the present work, the ultraviolet absorption spectrum of 5-methylpyrimidine in the vapour phase has been recorded in the range  $\lambda$  3410-2300 Å and analysed. The spectrum was also recorded in methylecyclohexane solution and the  $f$  values obtained. Since data on the ground state vibrational frequencies of the molecule is not available in the literature, the infrared absorption spectrum is also recorded and analysed. A preliminary note reporting the result of our investigation of the ultraviolet absorption spectra in the vapour state of 5-methylpyrimidine has been published (Shashidhar & Rao 1973). In this paper are reported the details of the investigation.

### 2. EXPERIMENTAL

Pure samples were distilled before use under reduced pressure. Vapour phase spectra were recorded with DK2A Beckmann recording spectrophotometer with 1 to 10 cm cells at room temperature and also with a medium quartz spectrograph with 10 to 200 cm cells at  $-10^\circ\text{C}$  to  $150^\circ\text{C}$ . Ilford R-40 plates were used. The accuracy of measurements has been estimated to be  $\pm 5\text{ cm}^{-1}$  for sharp bands and  $\pm 10\text{ cm}^{-1}$  for broad or diffuse bands. The solution spectra were recorded with the DK2A Beckman recording spectrophotometer and the  $f$  values of the solution spectrum were computed by the use of the equation.

$$f = 0.432 \times 10^{-8} MC^{-1}l^{-1} \int_{\nu_1}^{\nu_2} A(\nu)d\nu$$

where  $M$  is the molecular weight,  $C$  is the concentration in  $\text{g.l}^{-1}$ , where  $l$  is the cell length in cm and  $A$  is the absorbance  $\log(I_0/I)$ . The infrared absorption

spectrum of the molecule was recorded using a Parkin-Elmer model 221 double beam automatic spectrophotometer equipped with NaCl optics in the pure liquid state.

### 3. RESULTS AND DISCUSSION

The ultraviolet absorption spectrum of this molecule lies in the region  $\lambda$  3410–2300 Å. Two band systems were recorded for this molecule, one in the region, 29350–36517  $\text{cm}^{-1}$  (system I) and the other in the region 39080–42722  $\text{cm}^{-1}$  (system II).

The infrared frequencies are given in table 1. The analyses of the infrared spectrum were made by comparison with the parent molecule, pyrimidine (Sbrana *et al* 1966, Foglizzo & Novak 1967, Lord *et al* 1957). The characteristic contours were used to identify the species. If we assume  $C_{2v}$  symmetry for this

Table 1. Infrared frequencies of 5-methylpyrimidine in the pure liquid state.

Wave number in $\text{cm}^{-1}$ & intensity	Probable	Assignment
630 s	$b_2$	$\nu_{10b}$
725 vs	$b_1$	$\nu_4$
800 m	$b_1$	$\nu_{11}$
815 ms	$a_1$	$\nu_{12}$
885 ms	$b_1$	$\nu_5$
980 mb	$\text{CH}_3$	rocking
1045 ms	$a_1$	$\nu_1$
1120 m	$a_1$	$\nu_{9a}$
1165 s	$b_2$	$\nu_{15}$
1198 s	$b_2$	$\nu_3$
1242 s	$a_1$	$\nu_{13}$
1345 w	$b_2$	$\nu_{14}$
1385 sh	$\text{CH}_3$	symmetric bending
1405 vs	$a_1$	$\nu_{19a}$
1435 m	$\text{CH}_3$	asymmetric bending
1465 m	$b_2$	$\nu_{16b}$
1565 vs	$a_1$	$\nu_{9a}$
1585 vs	$b_2$	$\nu_{8b}$
2865 m	$\text{CH}_3$	symmetric stretching
2920 m	$\text{CH}_3$	asymmetric stretching
2980 m	$\text{CH}_3$	asymmetric stretching
3005 sh	$a_1$	$\nu_{20a}$
3025 m	$a_1$	$\nu_2$
3050 sh	$b_2$	$\nu_{7b}$

molecule, taking  $\text{CH}_3$  as an atomic point then 5-methylpyrimidine will have 24 normal modes of vibration with the distribution  $9a_1 + 2a_2 + 5b_1 + 8b_2$ .

*System I*: The band system lying in the region  $\lambda$  3410–2730 Å consists of narrow bands which are degraded to the red. This corresponds to the  $B_1 \leftarrow A_1(\pi^* \leftarrow n)$  transition in pyrimidine. The spectrum has been analysed with the help of the infrared data and also by the analysis of the corresponding spectrum of pyrimidine. As the temperature is varied from  $-10^\circ\text{C}$  to  $150^\circ\text{C}$ , the bands on the longer wavelength side of the band at  $30796\text{ cm}^{-1}$  increase in number and intensity. At still higher temperatures continuous absorption begins to set in. This study of temperature effect on band system has facilitated the choice of the band at  $30796\text{ cm}^{-1}$  as the 0, 0 band. Most of the bands could be accounted for in terms of 3 ground state fundamentals 555, 807 and  $1032\text{ cm}^{-1}$ , 4 upper state fundamentals 526, 785, 1001 and  $1020\text{ cm}^{-1}$  and two sequence intervals  $-143$  and  $-257\text{ cm}^{-1}$ . The first three fundamentals of the excited state 526, 785 and  $1001\text{ cm}^{-1}$  corresponding to the ground state fundamentals 555, 807 and  $1032\text{ cm}^{-1}$  are progressive forming and they may respectively correspond to the modes  $\nu_{6a}$ ,  $\nu_{12}$  and  $\nu_1$ . The upper state fundamental  $1020\text{ cm}^{-1}$  probably represent, the totally symmetric mode  $\nu_{8a}$ . Of the two observed sequence intervals  $-143$  and  $-257\text{ cm}^{-1}$ ,  $-143\text{ cm}^{-1}$  will probably represent, as suggested by Innes *et al* (1969), the 1-1 band of  $\nu_{16b}$  and  $-257\text{ cm}^{-1}$  the 1-1 band of some other fundamental, most probably  $\nu_{6b}$ , (the notation used here are the same as those used by Innes *et al* 1967). The wave numbers of the bands, the visual estimates of their relative intensities and their assignments were given in the earlier paper (Shashidhar & Rao 1973).

In the absorption spectra of 5-methylpyrimidine in the solution of methylcyclohexane, the strong band at  $31661\text{ cm}^{-1}$  has been chosen as the 0, 0 band (although the shift is large with respect to the 0, 0 band in vapour). It is interesting to note that the absorption spectrum of this compound in solution retain the vibrational structure observed in the corresponding vapour spectrum. Table 3 gives the spectral data of this molecule in solution.

*System II*: The spectrum for this system in vapour phase was recorded in the spectrophotometer. The band system in the region consists of broad and diffuse bands and are distinctly different from the sharp bands due to system I. This system corresponds to the  $\pi-\pi^*$  transition in pyrimidine. The band at  $39081\text{ cm}^{-1}$  has been chosen as the 0, 0 band of the system. Most of the bands could be analysed in terms of 4 upper state fundamentals 542, 795, 967 and  $1021\text{ cm}^{-1}$ . They may correspond to  $\nu_{6b}$ ,  $\nu_{12}$ ,  $\nu_1$  and  $\nu_{8a}$  modes respectively. The band data and their assignment are given in table 3.

The data corresponding to the absorption spectrum in solution of 5-methylpyrimidine are given in table 2.

Table 2. Ultraviolet absorption bands of 5-methylpyrimidine in methyleyclohexane (concentration : 0.15 gm/lt  $n-\pi^*$  transition)

Wave number in $\text{cm}^{-1}$ and intensity	Assignment
30642 m	0,0-1019
31192 m	0,0-2 $\times$ 224
31437 sh	0,0-224
31661 s	0,0
32219 m	0,0+558
32670 s	0,0+1009
33230 m	0,0+1009+558
33471 m	0,0+2 $\times$ 1009-224
33680 s	0,0+2 $\times$ 1009
34242 s	0,0+2 $\times$ 1009+558
34479 w	0,0+3 $\times$ 1009-224
34712 w	0,0+3 $\times$ 1009
35262 w	0,0+3 $\times$ 1009+558
36236 w	0,0+4 $\times$ 1009+558
$f_s = 0.135 \pm 0.002$ $\pi-\pi^*$ transition (concentration : 0.02 gm/lt)	
38823 s	0,0
39749 s	0,0+926
40663 s	0,0+2 $\times$ 926
41583 sh	0,0+3 $\times$ 926
$f = 0.055 \pm 0.002$	

Table 3. Ultraviolet absorption bands of 5-methylpyrimidine in the vapour state ( $\pi-\pi^*$  transition).

Wave number in $\text{cm}^{-1}$ and intensity	Assignment
39801 s	0,0
39203 w	---
39623 sh	0,0+542
39876 w	0,0+795
40048 s	0,0+967
40102 s	0,0+1021
40416 m	0,0+795+542
40853 m	0,0+795+967
40887 s	0,0+1021+795
41022 s	0,0+2 $\times$ 967
41139 m	0,0+2 $\times$ 1021
41607 s	0,0+2 $\times$ 967+542
42004 m	0,0+3 $\times$ 967
42722 w	0,0+3 $\times$ 967+795

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