

## Electronic and vibrational spectra of 2,4,6-trichloro- and 6-chloro-2,4-dimethoxypyrimidine

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**Abstract.** This paper presents the investigations of the electronic and vibrational spectra of 2,4,6-trichloropyrimidine and 6-chloro 2,4-dimethoxypyrimidine. The electronic spectra have been recorded in the liquid and vapour states in the region  $50000\text{--}28000\text{ cm}^{-1}$ . The  $n\text{-}\pi$  and  $\pi\text{-}\pi$  transitions are classified in each case. Infrared absorption spectra of 2,4,6-trichloropyrimidine in nujol have been recorded in the region  $4000\text{--}400\text{ cm}^{-1}$ . It is concluded that substituents like Cl or  $\text{OCH}_3$  do not have much influence on the  $sp^2$  electron of the nitrogen atom of the ring. From infrared studies the mass-dependent modes and the modes insensitive to substitution have been pointed out. The assignments are tentative and are based on the group frequency approach and data available for similar molecules.

**Keywords.** UV and IR spectra; 2,4,6-trichloropyrimidine; 6-chloro-2,4-dimethoxypyrimidine.

### 1. Introduction

Amongst the three diazines, light absorption studies of pyridazine, pyrazine and their substituted analogues have been made purely for spectroscopic purpose. Thymine, cytosine and uracil are substituted pyrimidines and are well known for their biological activity. In the case of pyrimidine and substituted pyrimidines, the aim is two-fold. Spectroscopic interest apart, investigations have also been carried out on their biological activity by many workers. The role of substituents in pyrimidines is very important. In earlier investigations on di- and tri-substituted pyrimidines (Srivastava and Rohitashava 1981; Srivastava and Prasad 1982; Srivastava *et al* 1984, 1985), tautomeric structures have been reported with OH,  $\text{NH}_2$  and SH groups arranged at different positions on the ring and their spectra interpreted in terms of the proposed structures. For the present, we have selected two molecules, 2,4,6-trichloropyrimidine and 6-chloro 2,4-dimethoxypyrimidine, to study the effect of substitution on the  $\pi\text{-}\pi$  and  $n\text{-}\pi$  systems of pyrimidine. If the substituents act as electron donors a blue shift of the  $n\text{-}\pi$  system will be observed, since they stabilize the ground state more than the upper state. Substituents which can act as electron acceptors behave quite differently and produce larger stabilization in the excited state than in the ground state and cause a red shift of the  $n\text{-}\pi$  bands. In addition, the infrared absorption spectra of both molecules have been recorded and the observed bands are interpreted in terms of ring vibrations and vibrations associated with the substituent groups/atoms.

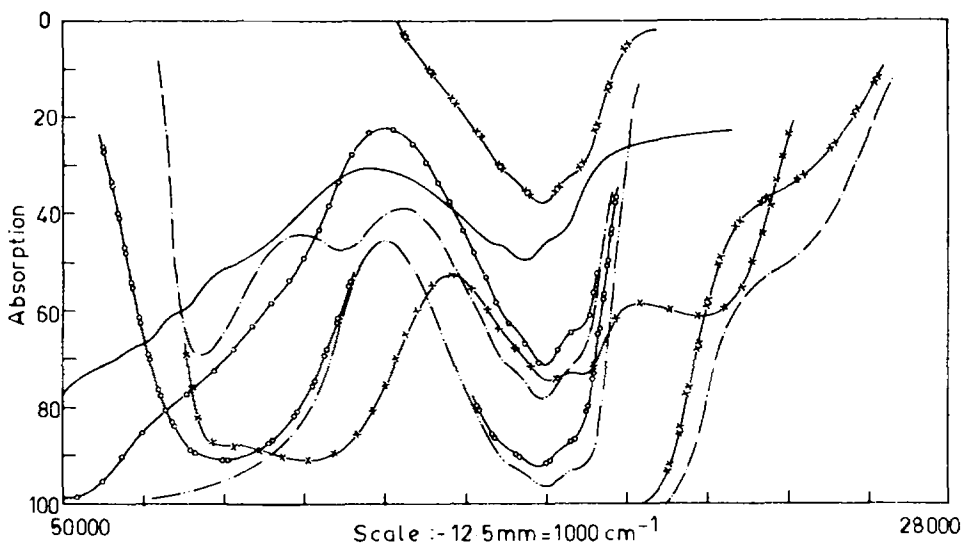
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## 2. Experimental

Attempts were made to photograph the absorption spectra on a Hilger medium quartz spectrograph in the vapour phase but no discrete bands could be obtained for either of the two molecules. Hence, we recorded the electronic spectra in vapour and liquid states with absorbing path lengths of 5 and 1 cm, respectively, on a Carl Zeiss UV-VIS double beam spectrophotometer in the region  $50000\text{--}28000\text{ cm}^{-1}$ . For obtaining the required amount of vapour for absorption, the tube was heated upto  $50^\circ\text{C}$ . The spectra in the liquid state recorded at room temperature are shown in figures 1 and 2. An analysis of the bands along with their correlation with pyrimidine and a few monosubstituted pyrimidine is presented in tables 1 and 2, respectively, for the two molecules. The accuracy of measurement of these bands is  $\pm 40\text{ cm}^{-1}$ . The infrared absorption spectrum of 2,4,6-trichloropyrimidine was recorded in the vapour phase with a gas cell of path length 10 cm. The band contours could not be recorded. For 6-chloro-2,4-dimethoxypyrimidine the nujol mull technique was employed. The infrared spectra of both the molecules recorded in the region  $4000\text{--}400\text{ cm}^{-1}$  on a Carl Zeiss Specord 75 IR are shown in figures 3 and 4. The accuracy of measurement for these bands is upto  $\pm 7\text{ cm}^{-1}$ .

## 3. Discussion

Substitution of chlorine atoms at the 2,4 and 6-positions in pyrimidine, which is 1,3-diazine, does not alter the symmetry of the parent molecule. Hence, the  $C_{2v}$  point group has been ascribed to this molecule. On the other hand, the  $C_s$  point group has been ascribed to 6-chloro-2,4-dimethoxypyrimidine as there is no plane of symmetry other than that containing all the atoms.



**Figure 1.** UV absorption spectra of 2,4,6-trichloropyrimidine in vapour (—), dioxane (---), water (- - -), N/10 sodium hydroxide (- x -), N/10 sulphuric acid (- o -), chloroform (- x x -), methyl alcohol (- o o -).

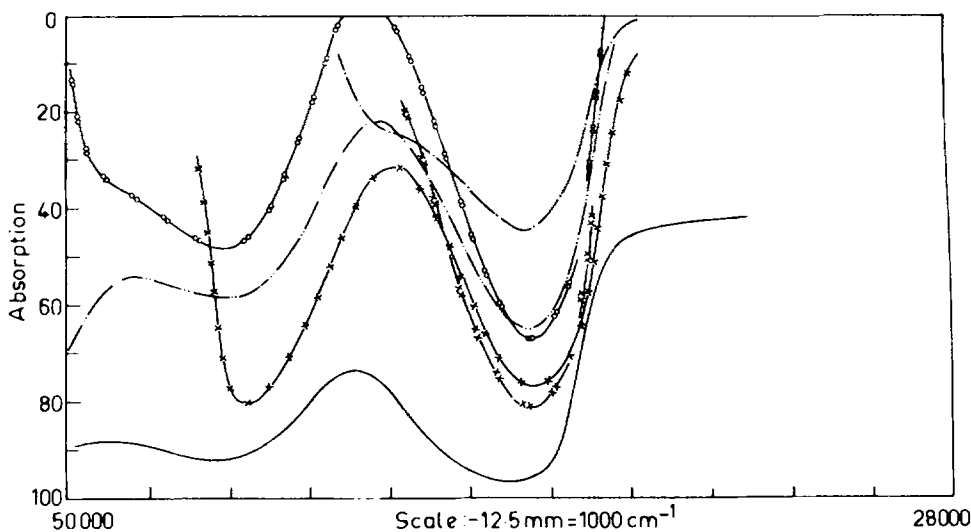


Figure 2. UV absorption spectra of 6-chloro-2,4-dimethoxy pyrimidine (explanation of symbols as in figure 1).

### 3.1 Electronic spectra

The vapour absorption spectra of 2,4,6-trichloropyrimidine show two absorption systems originating from  $\pi$ - $\pi$  transitions. The analysis of the second  $\pi$ - $\pi$  system shows the presence of  $\nu_{12}$ , the ring-bending mode ( $880\text{ cm}^{-1}$ ). This system appears with structure in all the solvents. In view of the accuracy of the bands it appears that the  $\nu_{12}$  mode is excited. The first  $\pi$ - $\pi$  system shows some structure in the vapour phase as well as in methyl alcohol but no analysis could be proposed because vibrational analyses at large energies are always doubtful due to the involvement of a large number of energy levels.

In addition to the  $\pi$ - $\pi$  system, a transition due to the nonbonded electron of the ring nitrogen atom has also been found in solvents like dioxane, N/10 sodium hydroxide, chloroform and methyl alcohol. As expected, this system disappears in acidic solutions. The  $n$ - $\pi$  and  $\pi$ - $\pi$  systems show a blue and red shift respectively. This is in accordance with the general observations for such molecules (table 1). The intensities of the  $\pi$ - $\pi$  transitions are greater as compared to the  $n$ - $\pi$  transitions. In addition to the above transitions a band at  $45200\text{ cm}^{-1}$  in the vapour phase, at  $43000\text{ cm}^{-1}$  in dioxane and at  $43800\text{ cm}^{-1}$  in N/10 sodium hydroxide, has been located. In the absence of any data no positive explanation for these bands could be made. In the electronic spectra of 6-chloro-2,4-dimethoxypyrimidine, one  $n$ - $\pi$  and two  $\pi$ - $\pi$  transitions have been classified. These show no structure either in the vapour phase or in solution. The presence of the  $n$ - $\pi$  system has been noticed only in dioxane. The shift of the  $\pi$ - $\pi$  and  $n$ - $\pi$  systems follows the general pattern reported in the literature (table 2). These investigations lead to the conclusion that groups like Cl or  $\text{OCH}_3$ , when substituted around the ring show a blue shift in the case of  $n$ - $\pi$  transitions and a red shift in the case of  $\pi$ - $\pi$  transitions. Further, the substituents act as electron donors and stabilize the ground state more than the excited state.

**Table 1.** Ultraviolet absorption spectra of 2,4,6-trichloropyrimidine in the liquid and vapour states in the region 50000–28000  $\text{cm}^{-1}$  and its correlation with pyrimidine and a few substituted pyrimidine

Molecule	Solvent	First $\pi$ - $\pi$ system	Second $\pi$ - $\pi$ system	$n$ - $\pi$ system	Assignment	Reference
Pyrimidine	Cyclohexane	53000	41000	33600		Stern and Timmons 1970
	Water	53200	41600	37400		
	Ethylalcohol	—	41000	35800		
2-Chloropyrimidine	Water	47800	39800	—		Rao 1961
	Water	47400	38800	—		
5-Chloropyrimidine	Neutral solution	—	38597	—		Present work
2,4,6-Trichloropyrimidine	Vapour	46960, 47880, 48680	37600, 38480, 39360	—	37600 = 0, 0 band 38480 = 0, 0 + 880 39360 = 0, 0 + 2 × 880	
Dioxane	Dioxane	46560	37200, 38080, 39040	31840	37200 = 0, 0 band 38080 = 0, 0 + 880 39040 = 0, 0 + 2 × 880	
Water	Water	—	37080, 38000, 38960	—	37080 = 0, 0 band 38000 = 0, 0 + 920 38960 = 0, 0 + 2 × 920	
N/10 sodium hydroxide	N/10 sodium hydroxide	46320	36880, 37880	34000	36880 = 0, 0 band 37880 = 0, 0 + 1000	
N/10 sulphuric acid	N/10 sulphuric acid	—	37080, 38000, 39000	—	37080 = 0, 0 band 38000 = 0, 0 + 920 39000 = 0, 0 + 2 × 920	
Chloroform	Chloroform	—	37160, 38080, 39000	31680	37160 = 0, 0 band 38080 = 0, 0 + 920 39000 = 0, 0 + 2 × 920	
Methylalcohol	Methylalcohol	45800, 46560	37240, 38160, 39120	32000	37240 = 0, 0 band 38160 = 0, 0 + 920 39120 = 0, 0 + 2 × 920	

All values are in  $\text{cm}^{-1}$

**Table 2.** Ultraviolet absorption spectra of 6-chloro-2,4-dimethoxypyrimidine in the liquid and vapour states in the region 50000–28000  $\text{cm}^{-1}$  and its correlation with pyrimidine and a few substituted pyrimidine

All values are in  $\text{cm}^{-1}$

Molecule	Solvent	All values are in $\text{cm}^{-1}$			Reference
		First $\pi$ - $\pi$ system	$n$ - $\pi$ system	Second $\pi$ - $\pi$ system	
Pyrimidine	Cyclohexane	53000	33600	41000	Stern and Timmons 1970
	Water	53200	37400	41600	
	Ethylalcohol	—	35800	41000	
2-chloropyrimidine	Water	47800	—	39800	Jaffe and Orchin
5-chloropyrimidine	Water	47400	—	38800	
2-methoxypyrimidine	Cyclohexane	47604	33888	37868	Jaffe and Orchin
4-methoxypyrimidine	Cyclohexane	46497	37026	40310	
6-chloro-2,4-dimethoxy-pyrimidine	Vapour	46320	—	39000	Present work
	Dioxane	—	42320	38560	
	Water	46000	—	38480	
	N/10 Sodium hydroxide	45560	—	38320	
	N/10 Sulphuric acid	46000	—	38320	
	Chloroform	—	—	38480	
	Methyl alcohol	46080	—	38400	

### 3.2 Vibrational spectra

Both the molecules in the present study are trisubstituted pyrimidines. Only one C–H bond is present in each case. Vibrations of this bond involve C–H out of plane and in plane bending, and stretching modes. In the case of nearly all the aromatic molecules, the vibrations associated with the C–H bond and the functional groups are almost free of any influence of the substituents. With this in mind, the vibrations associated with the C–H bond and the attached functional groups of each molecule have been identified and presented in table 3.

The infrared absorption spectra of pyrimidine contain four bands at 1400, 1461, 1569 and 1610  $\text{cm}^{-1}$ . These bands are analogous to the components of the  $e_{1g}$ , 1485 and  $e_{2g}$ , 1595  $\text{cm}^{-1}$  modes of benzene. Spectra of substituted pyrimidines show that these vibrations are almost insensitive to substitution. Hence, the two pairs of bands at 1407 and 1433 and 1533 and 1560  $\text{cm}^{-1}$  in 2,4,6-trichloropyrimidine and at 1400 and 1480  $\text{cm}^{-1}$  and 1567 and 1580  $\text{cm}^{-1}$  in 6-chloro-2,4-dimethoxypyrimidine have been assigned, respectively, to the  $\nu_{19}$  mode and  $\nu_8$ , the ring stretching mode.

Sabrana *et al* (1967) studied the spectra of pyrimidine and some of its deuterated analogues and have suggested that the ring breathing  $\nu_1$  mode is mass-dependent. Similar observations have been made in the spectra of trisubstituted benzenes also. Thus the strong bands at 833 and 827  $\text{cm}^{-1}$  in the two respective molecules have been assigned to the  $\nu_1$  mode. The other ring vibrations which are not very sensitive to substituent effects are  $\nu_{12}$  and  $\nu_{14}$  modes. These are assigned and presented in table 3. The  $\nu_6$  mode which represents the ring-bending mode has been found to be mass-dependent by Sabrana *et al* (1967). This observation is true for substituted benzenes also. On the basis of data for trisubstituted benzenes, the pair of bands at 573 and 613  $\text{cm}^{-1}$  in 2,4,6-trichloropyrimidine and at 600 and 633  $\text{cm}^{-1}$  in 6-chloro-2,4-dimethoxypyrimidine have been assigned to the  $\nu_6$  mode.

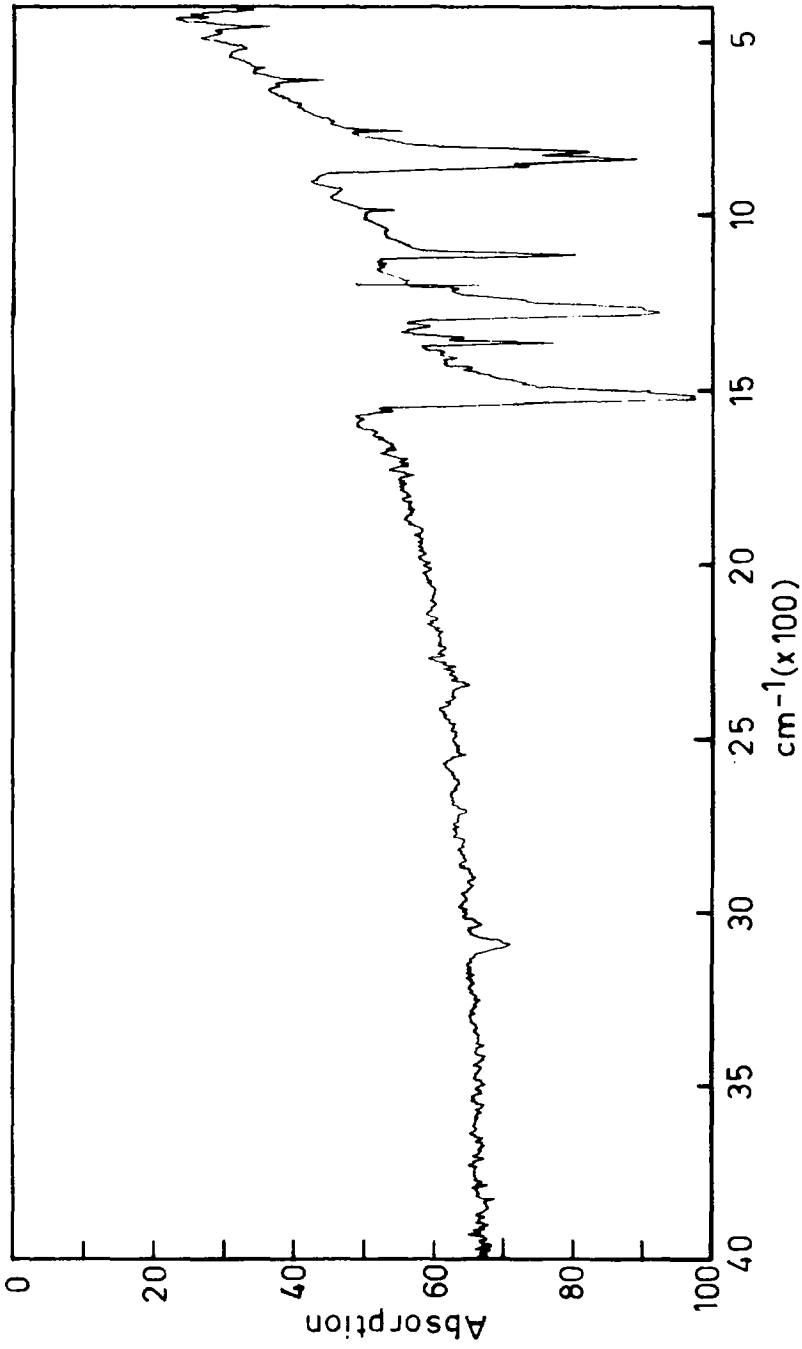


Figure 3. IR absorption of 2,4,6-trichloropyrimidine in vapour in the region 4000-400 cm<sup>-1</sup>.

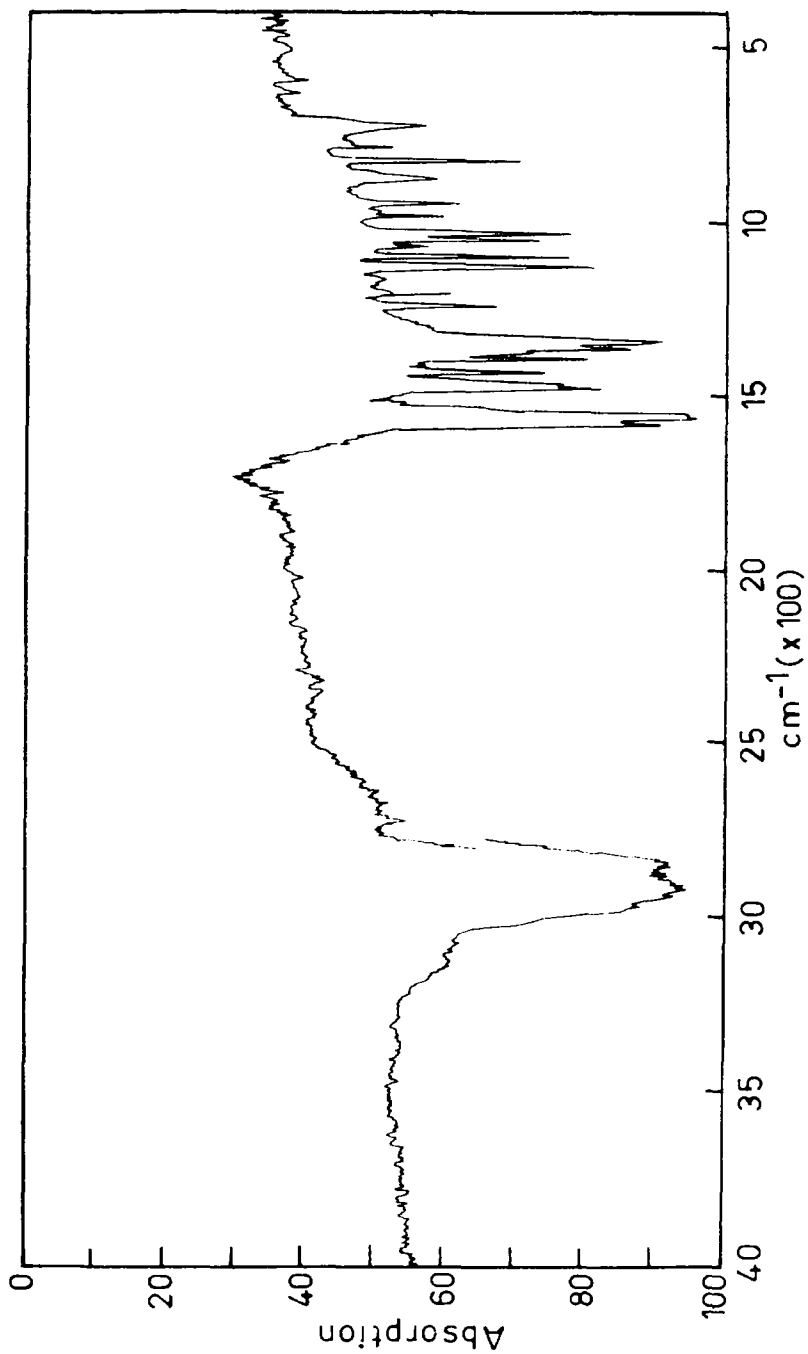


Figure 4. IR absorption of 6-chloro-2,4-dimethoxy pyrimidine in nujol in the region 4000-400  $\text{cm}^{-1}$

**Table 3.** Correlation of fundamental vibrational frequencies of 2,4,6-trichloropyrimidine and 6-chloro-2,4-dimethoxypyrimidine with pyrimidine and their modal assignment.All values are in  $\text{cm}^{-1}$ 

Pyrimidine	2,4,6-trichloro-pyrimidine in the vapour phase	6-chloro-2,4-dimethoxy pyrimidine in nujol	Assignment
394	433 (w)	467 (w)	$\nu_{16}$
—	460 (ms)	—	} $\beta$ (C-Cl)
—	473 (w)	500 (w)	
624	573 (vw)	600 (w)	
677	613 (ms)	633 (w)	$\nu_6$
679	680 (w)	688 (w)	$\nu_4$
—	733 (vw)	727 (ms)	} $\nu$ (C-Cl)
—	760 (s)	—	
990	833 (vvs)	827 (s)	$\nu_1$
806	813 (vs)	—	$\gamma$ (C-H)
870	—	873 (m)	$\gamma$ (C-H)
1065	1040 (w)	1033 (s)	$\nu_{12}$
1071	1113 (vs)	1100 (s)	$\beta$ (C-H)
—	—	1126 (s)	$\nu$ (C-OCH <sub>3</sub> )
1291	1280 (vs)	1240 (ms)	$\nu_{14}$
—	—	1367 (s)	CH <sub>3</sub> sym bending
—	—	1433 (s)	CH <sub>3</sub> asym bending
1400	1407 (w)	1400 (s)	} $\nu_{19}$
1461	1433 (w)	1480 (s)	
1569	1533 (vs)	1567 (s)	} $\nu_8$
1610	1560 (w)	1580 (s)	
—	—	2853 (w)	$\nu$ (C-H) aliphatic
—	—	2913 (w)	$\nu$ (C-H) aliphatic
3001	3033 (w)	—	$\nu$ (C-H)
3085	—	3083 (w)	$\nu$ (C-H)

vs = very strong, s = strong, ms = medium strong, m = medium, w = weak;  $\nu$  = stretching,  $\beta$  = in plane bending,  $\gamma$  = out of plane bending, asym = asymmetric, sym = symmetric.

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### References

- Jaffe H H and Orchin M 1965 *Theory and applications of ultraviolet spectroscopy* (New York: John Wiley and Sons) p. 379
- Rao C N R 1961 *Ultraviolet and visible spectroscopy* (London: Butterworths) p. 57
- Sabrina G, Adembri G and Califano S 1966 *Spectrochim. Acta* **22** 1831
- Srivastava S L and Rohitashava 1981 *Indian J. Phys.* **B55** 455
- Srivastava S L and Prasad M 1982 *Indian J. Phys.* **B56** 358
- Srivastava S L et al 1984 *Spectrochim. Acta* **A40** 675
- Srivastava S L, Prasad M and Singh H S 1985 *Indian J. Phys.* **B59** 29
- Stern E S and Timmons C J 1970 *Electronic absorption spectroscopy in Organic Chemistry* 3rd edn. (London: Edwards Arnold) p. 157