CHAPTER 7

VIBRATIONAL SPECTRA AND ANALYSIS OF
2, 4, 6-TRIAMINOPYRIMIDINE
7.1 INTRODUCTION

Amino acid, N-heterocyclic molecules like pyrimidine, cytosine, uracil and their derivatives are of considerable biological importance. The study of their vibrational spectra is important to get information on their molecular conformation. The vibrational spectrum and/or assignment of pyrimidine has been studied by several authors (only a few important references are cited as they are found to be numerous) (1-7). The first vibrational assignments for diazines was made by Ito et al (1) and then by Lord et al (2). Simmons and Innes (4) have proposed a new assignment for the $A_1$ fundamentals of pyrimidine from the investigation of vibronic bands of pyrimidine $-h_4$ and pyrimidine $-d_4$, and they have also measured the infrared and Raman intensities of the later compound. Sbrana et al (6) studied the infrared spectra of pyrimidine $-h_4$ and pyrimidine $-d_4$. For lack of enough information originating from band contours, they have also measured the crystal spectra in polarized light for both isotopomers and have proposed a revised assignment. Foglizzo and Novak (7) confirmed the reassignment of Sbrana et al (6) for all but one of the fundamentals investigating the infrared spectrum of pyrimidine at liquid nitrogen temperature (crystalline
state) and in nonpolar solvents (liquid phase). Innes et al (8, 9) preferred the assignment of Sbrana et al (6) to that of Foglizzo and Novak (7). Milani-Nejad and Stidham (10) prepared six of the eight different deuterated pyrimidines belonging to $C_{2v}$ symmetry and reported their liquid phase, Raman and liquid and vapour phase infrared spectra. They altered some assignments of earlier authors in order to achieve reasonable frequencies and product rule agreement. Bokobza-Sebagh and Zarembowitch (11) investigated the infrared and Raman spectra of pyrimidine and its pentachloroiridium (111) complex. Comparing the pyrimidine and its pentachloroiridium spectra, they reassigned some of the fundamentals of pyrimidine. Umemoto et al (12) reexamined the out-of-plane vibrational assignments of pyrimidine-$h_4$ and its perdeuterated isotopomer investigating the polarized Raman, time-resolved phosphorescence and polarized dark sublevel phosphorescence spectra and reassigned some fundamentals of both compounds. Shimada and Maehara (13) reexamined the assignment of the normal vibrations of pyrimidine on the basis of the polarization behaviour of the Raman bands. Investigating the polarized Raman spectrum of the pyrimidine single crystal, they confirmed basically the assignment of Milani-Nejad and Stidham (10) for the in-plane vibrations, but preferred the assignment of Umemoto et al (12) for the out-of-plane ones.
Allenstein et al (14) recorded the infrared and Raman spectra of mono-, di- and trimethyl - pyrimidine and of mono- and dimethyl -S- triazine in benzene and CC14 from 100-4000 cm\(^{-1}\) and bonds have been assigned. They have compared the spectroscopic data of these compounds with those of the methyl substituted derivatives of benzene and pyridine.

Again Allenstein et al (15) recorded the infrared and Raman spectra of 4, 6 -dihalogenpyrimidine, 2, 4 -dihalogen-S-triazin, 2, 4, 6-trihalogenpyrimidine and 2, 4, 6-trihalogen -S-triazin (halogen = Cl, Br) in the range 100-4000 cm\(^{-1}\). A complete set of assignments for the fundamental vibrations for all compounds have been suggested based on \(C_{2v}\) and \(D_{3h}\) symmetry respectively.

Over the past few years normal coordinate calculations have been carried out for the planar modes of uracil and cytosine and assignments have been reported for a total of six isotopic analogs. Sasi and Ard (16) have examined the spectra of thymine, 1-methyl thymine and 1-methyluracil and a total of ten isotopic species of five pyrimidine derivatives. Inspite of considerable biological importance of the N- heterocyclic compounds like pyridine, cytosine and their derivatives very little spectroscopic studies are reported in the literature (17, 18). 2, 4, 6 -
triaminopyrimidine and 5 - methyl cytosine molecules which have considerable importance have not been studied in detail so far. Due to their complexity and low symmetry, it is difficult to interpret the spectra of such biological molecules with only infrared or Raman spectroscopy. By keeping this in mind, the study of Raman spectrum of 2, 4, 6-triaminopyrimidine has been undertaken in the present investigation along with the infrared spectrum. A complete spectroscopic information and vibrational analysis of 2, 4, 6-triaminopyrimidine are provided in this chapter.

7.2 EXPERIMENTAL

Pure chemicals of 2, 4, 6-triaminopyrimidine obtained from M/s Tokyo Kesai Kogyo Co. Ltd., Tokyo was used as such without further purification to record Raman and infrared spectra. The laser Raman spectrum of 2, 4, 6-triaminopyrimidine was recorded using 488 nm line of argon ion laser for excitation in the region 100-4000 cm⁻¹ in Cary model grating spectrophotometer with a 4W Ar⁺ laser. The infrared absorption of this compound was also recorded in the region 250-4000 cm⁻¹ on Perkin-Elmer spectrophotometer 521 in KBr pellet. The frequency for all sharp bands are accurate to ± 1 cm⁻¹. The observed bands along with their intensities and their proposed assignments are presented in
FIG-1 STRUCTURE OF 2,4,6-TRIAMINOPYRIMIDINE
FIG-2. INFRARED SPECTRUM OF 2,4,6-TRIAMINOPYRIMIDINE
FIG-3
LASER RAMAN SPECTRUM OF 2,4,6-TRIAMINOPYRIMIDINE

RAMAN INTENSITY (ARB UNITS)

WAVE NUMBER (CM\(^{-1}\))

3500
3000
2500
2000
1500
1000
500

table 1. The structure of the compound and the observed infrared and Raman spectra of the titled compound are shown in fig.1-3 respectively.

The bond lengths and bond angles were taken from Sutton's table. The normal coordinate calculations were performed using the programme given by Schachtschneider (19). Internal coordinates for the out-of-plane torsional vibrations were defined as recommended by IUPAC. The general quadratic valence force field was adopted for both in-plane and out-of-plane vibrations. The initial force constants were taken from similar trisubstituted benzene derivatives (20).

7.3 RESULTS AND DISCUSSION

The structure of several pyrimidine compounds have been determined (21, 22) and in all cases the molecules are found to be planar. Assuming NH₂ groups as single mass point, the present molecule, 2, 4, 6 - triaminopyrimidine belongs to C₂ᵥ point group symmetry and its 24 normal vibrations are distributed as 9A₁+8B₂+2A₂+5B₁. Apart from these 24 vibrations, there are 18 group vibrations that are active in both, Raman and infrared, except those belonging to symmetry species A₂, which are only Raman active. Assignments have been made on the basis of intensities and
magnitudes of the frequency in the infrared and Raman spectra, as well as from the normal coordinates analysis of the molecules.

7.3.1 C-H VIBRATIONS

Usually the bands around 3000 cm\(^{-1}\) are assigned to C-H stretching vibrations. They are not appreciably altered by the nature of substituents. Hence the strong band at 3109 cm\(^{-1}\) in 2, 4, 6-triaminopyrimidine is assigned to C-H stretching mode. Further, the substituted benzene gives rise to C-H in-plane bending and C-H out-of-plane bending modes. They are assigned to 1159 cm\(^{-1}\) (B\(_2\) species) and 775 cm\(^{-1}\) (B\(_1\) species), respectively. The C-H out-of-plane bending vibrations observed in the present work agree favourably with the band at 811 cm\(^{-1}\) in pyrimidine molecule. They are in good agreement with literature values (23).

7.3.2 C-NH\(_2\) VIBRATIONS

In this molecule one expects three C-NH\(_2\) stretching vibrations. The very strong bands at 1319 cm\(^{-1}\) and at 1245 cm\(^{-1}\) are assigned to C-NH\(_2\) stretching mode of B\(_1\), A\(_1\) and B\(_2\) species respectively. The normal coordinate analysis helps in assigning the band at 1245 cm\(^{-1}\) to C-NH\(_2\) stretching (A\(_1\) species). The results of normal coordinate
analysis was also used to assign the bands at 395, 354, 295 cm$^{-1}$ to $B_1$, $A_2$ and $B_1$ species respectively. These observations agree with Green (24), who suggested that the $X$-sensitive vibration for the C-NH$_2$ out-of-plane bending generally lies around 200 cm$^{-1}$. The bands at 386, 376 and 325 cm$^{-1}$ are assigned to C-NH$_2$ in-plane bending of $B_2$ and $A_1$ species, respectively. These observations are in line with Padhya and Bhujle (25).

7.3.4 RING VIBRATIONS

Benzene has two doubly degenerate modes $e'_{2g}$ (1596 cm$^{-1}$) and $e_{1u}$ (1485 cm$^{-1}$) and two non-degenerate modes, $b'_{2u}$ (1310 cm$^{-1}$) and $a'_{1g}$ (995 cm$^{-1}$) due to skeletal C-C stretching vibrations. The bands between 1400 and 1650 cm$^{-1}$ in benzene derivatives are assigned to these modes. The actual positions are determined, not so much by the nature of the substituents, but rather by the form of the substitution around the ring. The two bands observed at 1470 and 1440 cm$^{-1}$ are assigned to $A_1$ and $B_2$ species of C-C stretching vibrations. Present conclusion agrees well with Eggers and Lingren (26). The four more ring stretching vibrations 1861 and 1570 cm$^{-1}$, 1560 and 796 cm$^{-1}$ belonging to C-N stretch are assigned to $A_1$ species and $B_2$ species, respectively.
The in-plane carbon bending vibrations are derived from non-degenerate $b_{1u}$ mode of benzene. Hence very strong band at 980 cm$^{-1}$ is assigned to C-C-C in-plane bending mode. The carbon out-of-plane bending vibrations are derived from the non-degenerate $b_{2g}$ and degenerate $e_{2u}$ modes of benzene. The band observed at 578 cm$^{-1}$ is assigned to C-C-C out-of-plane vibrations.

**NH$_2$ GROUP VIBRATIONS**

The molecule under consideration possess three NH$_2$ groups and hence one expects three symmetric and three asymmetric N-H stretching vibrations. In all the primary aromatic amines the N-H stretching frequency occurs in the region 3300 - 3500 cm$^{-1}$ (27-29). The bands appearing at 3485, 3462, and 3420 cm$^{-1}$ are assigned to N-H asymmetric stretching vibrations while the bands at 3315, 3305 and 3210 cm$^{-1}$ are assigned to N-H symmetric stretching vibrations in NH$_2$ group. These observations agree very well with that of the literature values (30).

Bellamy (27) and Rao (31) suggested that the NH$_2$ scissoring modes lie in the region 1592 - 1650 cm$^{-1}$. In accordance with their conclusions, all the three NH$_2$ scissoring modes are identified at 1662, 1642 and 1595 cm$^{-1}$ in the present work. NH$_2$ twisting frequency is expected to
occur in the region 1060 cm\(^{-1}\). The bands observed at 1140, 1092 and 1041 cm\(^{-1}\) are assigned to NH\(_2\) twisting modes. This conclusion agrees favourably with earlier workers (32), who have assigned this mode at 1030 cm\(^{-1}\) in 2- aminomethyl pyrimidine. Similarly, the three NH\(_2\) wagging modes are identified at 670, 661 and 648 cm\(^{-1}\). These assignments agree very well with earlier workers (32, 33).

Evans (33) assigned the bands observed at 420 - 460 cm\(^{-1}\) in aniline as first overtone of NH\(_2\) torsional mode. In this present work, the weak bands observed in Raman spectra at 230, 222 and at 215 cm\(^{-1}\) are assigned to NH\(_2\) torsional modes. This agrees very well with Evans (33). The rest of the observed frequencies may be accounted for as resulting from the allowed combinations of the selective fundamentals, which give additional support for their choice.
<table>
<thead>
<tr>
<th>Species</th>
<th>Infrared frequency and intensity cm(^{-1})</th>
<th>Laser Raman frequency cm(^{-1})</th>
<th>Calculated frequency cm(^{-1})</th>
<th>Assignment/(PED%)</th>
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<td>-</td>
<td>-</td>
<td>3485 M</td>
<td>-</td>
<td>N-H asymmetric stretching in NH(_2) group</td>
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<tr>
<td>3460 S</td>
<td>3462 S</td>
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<td>3315 S</td>
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<td>N-H symmetric stretching in NH(_2) group</td>
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<tr>
<td>-</td>
<td>3305 M</td>
<td>-</td>
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<td>-</td>
<td>3210 S</td>
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<td>1642 W</td>
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<td>1470 W</td>
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B₂ 1430 VS 1440 S 1428 C-C stretching (92)
B₁ 1319 VS 1318 VS 1331 C-NHZ stretching (71)
A₁ 1244 VS 1245 VS 1254 C-NHZ stretching (91)
B₂ 1244 VS 1245 VS 1254 C-NHZ stretching (72)
B₂ 1159 VW - 1154 C-II in-plane bending (68)
1140 VW - - NH₂ twisting
1092 S 1098 M - NH₂ twisting
1041 M - - NH₂ twisting
B₂ 980 VS 982 VS 985 C-C-C in-plane bending (74)
B₂ 796 VS 796 VS 791 C-N stretching (87)
B₁ 780 Sh 775 M 775 C-H out-of-plane bending (95)
B₂ 719 M 720 VS 722 C-C ring breathing (60)
- 670 M - NH₂ wagging
- 661 M - NH₂ wagging
645 S 648 S - NH₂ wagging
A₂ - 578 M 571 C-C-C out-of-plane bending (59)
B₁ 540 S 540 S 546 NCN in-plane bending (55)
B₁ 392 M 395 M 386 C-NHZ out-of-plane bending (87)
B₂ 386 W 386 W 372 C-NHZ in-plane bending (84)
A₁ 370 W - - CNC in-plane bending (51)
A₁ 376 M 370 W 362 C-NHZ in-plane bending (74)
A₂ - 354 M 361 C-NHZ out-of-plane bending (90)
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<td>B₂</td>
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VS - Very strong;  
S - Strong;  
M - Medium;  
W - Weak;  
VW - Very weak;  
Sh - Shoulder.