Thermodynamic and Vibrational Spectral Analysis of 3,2,4,6 BTMA

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Abstract

The present research represent the vibrational assignments of 3-bromo-2, 4, 6-tri methyl aniline (Here after referred as 3, 2, 4, 6-BTMA) from it's infrared and Raman spectra. The thermodynamic properties of this molecule have also been computed. The infrared and Raman spectra of 3-bromo-2,4,6-tri methyl aniline have been reported .The spectra have been analyzed and assignments to the fundamental and group vibrations have been proposed .The effect of substituents has been discussed .The thermodynamic functions have been computed and discussed .

Keywords

Thermodynamics, Vibrational, Spectra, Analysis, BTMA, Heterocyclic.

Introduction

N-Heterocyclic molecules and their derivatives are of immense importance as they play a central role in the structure and properties of the important nucleic acids. The benzene ring system is very important as a structural unit in the natural products and compounds of pharmaceutical interest. It has been shown by Jesson et. Al [1] that pyridine molecule has planner structure in the ground state and quasi planar one in the excited state. Major part of the work on benzene derivatives regarding the spectral studies was tabulated by Wilmshurst, Bernstein [2], Innes and Co-workers [3]. Many workers [4, 5] also studied the vibrational spectra of biologically important benzene derivatives though the high complexity and low symmetry of these molecules have made the interpretation extremely difficult.

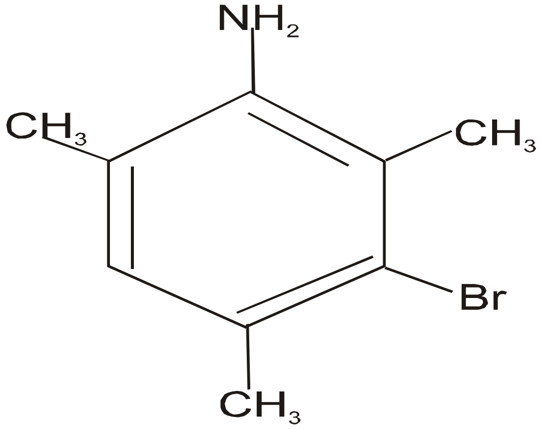
The vibrational spectrum of aniline has been studied by Evans [6]. The infrared spectra of a large number of mono-, di-, tri-, tetra-substituted anilines have been reported by several workers [7, 8, and 9] in solid phase and in various solvents. Raman spectra of the substituted anilines have been recorded and observed fundamentals compared with the infrared frequencies [9]. The present study reports the vibrational assignments of 3-bromo-2, 4, 6-tri methyl aniline (Here after referred as 3, 2, 4, 6-BTMA) from it's infrared and Raman spectra. The thermodynamic properties of this molecule have also been computed.

Experimental

The spec pure sample of 3, 2, 4, 6-BTMA was obtained from M/S EGA- CHEMIE WEST GERMANY and was used as such without further purification. It's purity was, however, confirmed by elemental analysis and melting point determination. The infrared spectra of 3,2,4,6-BTMA was recorded in the region 400-4000 cm^{-1} on Perkin Elmer Spectrophotometer model 52 using KBr pellet techniques. The laser Raman spectra of said molecule was recorded in the region 50-4000 cm^{-1} on Spex Rama Lab Spectrophotometer using 52 MW Argon krypton laser beam of wave length 488 nm. The frequencies of all the sharp bands are accurate to ± 1cm^{-1}.

Results and Discussion

The structural diagram is shown in fig.1.



The infrared and Raman spectra of 3, 2, 4, 6-BTMA are shown in fig.2 and 3. The observed fundamentals along with their assignments are entered in table 1. The statistically computed thermodynamic functions viz. enthalpy function, free energy function, entropy and heat capacity with absolute temperature are shown in table 2. The variation of enthalpy function and heat capacity with absolute temperature is shown in fig. 4 while the variation of free energy function and entropy with absolute temperature is shown in fig. 5.

Assuming CH_3 and $-NH_2$ groups as single mass point, the molecule 3,2,4,6-BTMA will belong to C_S symmetry and as such 30 normal modes will be distributed as ($11a_1 + 10b_2$) in plane (a') and ($3a_2 + 6b_1$) out of plane (a")vibrations .While all these modes are allowed in the Raman spectrum , but a_2 are infrared active . In addition, there are six internal CH_3 vibrations and six internal $-NH_2$ group vibrations. Thus, there will be a total of 42 fundamental vibrations in each molecule, which are discussed below:

Ring Vibrations

C – C Vibrations

It has been observed by Pitzer[10] and Padhya[11] that a group of four bands usually lie in the region 1400-1650 cm^{-1} which represent characteristic skeletal modes of the semi unsaturated C-C bonds . Two degenerate vibrations e_{2g} (1595 cm^{-1}) e_{1u} (1485 cm^{-1}) of benzene are responsible for these two bands [12, 13]. Under reduced symmetry c_s , the degeneracy is removed and split into two component vibrations .The infrared bands at 1545 , 1528 and 1474 cm^{-1} with the counter part of Raman band at 1550,1535 and 1485 have been assigned to ring stretching modes in the molecule 3,2,4,6-BTMA. The carbon vibration b_{2u}(1310 cm^{-1}) mode of benzene, which is known as Kekule mode, occurs in the region 1240-1290 cm^{-1} [14] .In view of this , the infrared band at 1316 cm^{-1} with the counter part of Raman band at 1349 cm^{-1}have been related to this mode of vibration in the present molecule . In benzene and it's derivatives the frequency of ring breathing mode has been assigned in the region 690- 920 cm^{-1}[15-18]. But Under reduced symmetry (c_s) the C-C ring breathing a_{1g} (995 cm^{-1}) and closely lying C-C-C trigonal bending b_{1u} (1010 cm^{-1}) vibration of benzene give rise to combine modes. As a result of which an appreciable interaction is possible. When the symmetry of the benzene ring is lowered due to the substitution, the breathing vibration occurs at greatly reduced frequency. This could be understood by the interaction of ring breathing mode with trigonal mode b_{1u}. Jackobson and Brewer [19] assigned the a_{1g} mode between 820-860 cm^{-1} while Goel and Agarwal [20] assigned this mode at 850 cm^{-1} in 4-methoxy-benzonitrile. Moreover , the a_{1g} mode being most symmetric gives rise to a very strong and polarized bend in the Raman spectra .During the present study , infrared bends at 802 cm^{-1} and 980 cm^{-1} with the counter part of Raman band at 800 and 1010 cm^{-1},in this molecule ,are related to the ring breathing and trigonal modes respectively . These assignment are in agreement with the literature values [6, 11, 21]. In the present case ,the infrared band at 731 cm^{-1} with counter part of Raman band at 755 cm^{-1} can also be assigned to the b_{2g} mode, while the infrared bands at 427 cm^{-1} with counter part of Raman band at 435 cm^{-1} have been assigned to e_{2u} mode in the present molecule 3,2,4,6-BTMA . These assignments are in agreement with the literature values [22].

C-H Vibrations

The nitrogen atom of aniline is isoelectric with the CH group. As there is little difference in mass or in the bond strengths to adjacent atoms. It is to be expected that the majority of the fundamental frequencies will be very close to those of benzene and the difference will only arise due to substituents attached to the ring.

According to Bellamy [15] and Colthup [16], this (C-H) stretching mode lies in the region 3000-3100 cm^{-1}.Also the aromatic structure show the presence of C-H stretching vibrations in the region 3000-3100 cm^{-1} [23] .These vibrations are highly characteristic of aromatic ring itself and afford a ready identification for this structure . In this region, the bands are not appreciably affected by the nature of the substituents. The C-H stretching frequencies in benzene derivatives arise from the modes a_{1g} (3073 cm^{-1}), e_{2g} (3046 cm^{-1}), b_{1u} (3060 cm^{-1}) and e_{1u} (3080 cm^{-1}) of benzene. The molecule 3, 2, 4, 6-BTMA is penta substituted benzene and only one hydrogen atoms is left in the ring. It may give rise to one C-H stretching vibrations, while other frequencies depend on the mass and nature of the substituents. In the present case, the infrared bend at 3012, 2976 cm^{-1} with counter part of Raman band at 3051 and 2916 cm^{-1} in the molecule have been assigned to C-H stretching modes. These assignments find support from the literature values [15, 24].

The C-H in plane bending modes appear in the region 1050-1175 cm^{-1} [15, 25, 78]. In view of this, the pair of infrared bends at 1147 and 1196 cm^{-1} with counter part of Raman band 1155 and 1205 cm^{-1} have been assigned to this mode. The C-H out of plane vibrations which are umbrella vibrations, are observed in the region below 1000 cm^{-1} . Sanyal et al. [27] have assigned C-H out-of-plane bending modes at 940 cm^{-1} .The infrared bands with strong intensity at 922 and 868 cm^{-1} with counter part of Raman band at 955 and 905 cm^{-1} are related to these umbrella vibrations in the molecule 3,2,4,6-BTMA. These vibrations are in accordance with the assignments made by previous workers [10, 15, 25-27].

From the data available in N-heterocyclic molecule [28, 29] the IR band observed at 3215 cm^{-1} (KBr) with the counter part of Raman band at 3208 cm^{-1}in the molecule 3, 2, 4, 6-BTMA may be assigned to N-H stretching mode. This is possible only when there is a proton migration from the ring. It can be infrared that in the said molecule, proton migration takes place from hydroxyl group to the nitrogen of the ring, giving rise to N-H stretching mode. The IR band observed at 1723 cm^{-1} (KBr) with the counter part of Raman band at 1715 cm^{-1}in the molecule 3,2,4,6-BTMA has been assigned to (N-H) in-plane bending mode which finds support from the literature [29,30].

C-X Vibrations

Kletz and Price[31] have suggested the occurrence of X-sensitive vibrations near 1300 cm^{-1} in substituted benzenes .The C-NH_2 stretching vibration occurs near 1300 cm^{-1}[20,15]. Evans [6] assigned this mode at 1278 cm^{-1} in aniline. In view of this, the infrared band at 1296 cm^{-1} with counter part of Raman band at 1301 cm^{-1} have been related to this mode. The C-NH_2 in-plane bending vibration has been assigned at 344 cm^{-1} in Raman spectrum. This mode, in infrared spectrum, could not be observed in 3, 2, 4, 6-BTMA. This fined support from the work of Sanyal ET. al. [32]. The frequency around 250 cm^{-1} has been assigned to C-NH_2 out of plane bending vibration by many workers [33]. However, a frequency of this magnitude could not be observed in infrared spectrum, while the Raman band at 238 cm^{-1} is related to this mode in the molecule 3,2,4,6-BTMA .

C-Br stretching modes have generally been assigned in between the range 750-550 cm^{-1}in the substituted benzenes [32, 33]. Due to the one bromo substitution, one C-Br stretching frequency is expected in the molecule 3,2,4,6-BTMA . In the present study, the Raman band at 750 cm^{-1} have been assigned to this stretching frequency .The C-Br in-plane bending vibration is observed at 290

cm^{-1} in Raman spectrum. However, the infrared band of such a magnitude could not be observed in the molecule 3, 2, 4, 6-BTMA. Green et. al. [34] have assigned frequencies between 110-200 cm^{-1} to C-Br out of plane bending vibrations in various bromo substituted benzenes. In the present study, infrared band could not be observed, while the Raman band at 117 cm^{-1} in the molecule has been assigned to this mode. These assignments have been supported by literature values [35, 36].

The molecule 3,2,4,6-BTMA has three methyl groups at 2, 4 and 6 positions, hence three C-CH_3 valance oscillations are expected. It has been shown by Colthup [16] that the C-CH_3 stretching vibrations appear in the range 1200-1300 cm^{-1}. In view of this, the IR band observed at 1316 cm^{-1} with the counter part of Raman band at 1349 cm^{-1} have been assigned to C-CH_3 stretching modes in the said molecule.

These assignments are supported by the literature [37].

Varsanyi et al. [38] displays the frequency of C-X in-plane-bending vibrations 300-500 cm^{-1} for aromatic ring. In the present study, the Raman bands observed at 344,365 cm^{-1} have been assigned to C-CH3 in-plane bending vibrations [39, 40, and 41].

Varsanyi et al. [38] further displays that the out-of-plane bending C-X vibrations for trisubstitution are lie in between 270-140 cm-1. In view of this, the Raman bands observed at 251,235 and 211 cm-1 have been assigned to C-CH3 out-of-plane bending mode, respectively (as in pyridine the nitrogen which has no hydrogen is counted as substituted carbon atom and the correlation used for benzene rings can then be applied[38,42,43] .

Group Vibrations

NH_2 Group Vibrations

Aniline molecule is presumably non-planer with NH_2 group inclined at nearly 30^{O} to the plane of benzene ring . In aniline Evans [6] has assigned frequencies at 3440, 3360, 1618, 1054, 670, and 490 cm^{-1} to the asymmetric stretching, symmetric stretching, and scissoring, twisting, wagging and first overtone of torsional modes of -NH_2 group respectively. Bellamy [15] and Cross [44] assigned the frequency range 3500-3000 cm^{-1} and 1650-1590 cm^{-1} for N-H stretching and scissoring modes respectively. Bellamy and Williams[45] have shown that symmetric and asymmetric stretching vibrations depend basically upon the same force constant therefore , they must be related with each other .They have found an empirical relation which connects the two stretching frequencies :

$$v_{sym} = 345.53 + 0.876\ v_{asym}$$

The higher frequency is attributed to the N-H asymmetric stretching modes and the lower one to the N-H symmetric mode .Under the present investigation the infrared bands at 3480 cm^{-1} and 3399 cm^{-1} with counter part of Raman band at 3474 and 3365 cm^{-1} have been assigned to N-H asymmetric and symmetric stretching modes respectively in 3,2,4,6-BTMA. The observed values obey the above empirical relation. The –NH_2 scissoring mode lies in between the region of C-C stretching modes and has been identified at 1622 cm^{-1} in the infrared spectrum and at 1630 cm^{-1} in the Raman spectrum of the investigated molecule .The infrared band at 1014 cm^{-1} with counter part of Raman band at 1045 cm^{-1} have been assigned as –NH_2 twisting mode in 3,2,4,6-BTMA.The strong intensity in Raman band at 673 cm^{-1} have assigned to the –NH_2 wagging mode in the same molecule .This mode could not be observed in the infrared spectrum of the molecule .The frequencies , at 427 cm^{-1} in the infrared spectrum and at 435 cm^{-1} in the Raman spectrum ,can also be related to the $-NH_2$ torsional mode in the compound 3,2,4,6-BTMA .

ch_3 Group

There are three C-H bonds in a methyl group so there will be three C-H stretching vibrations, out of which one is symmetric stretching vibration and the rest two are asymmetric stretching vibrations [42]. Fox and Martin [46] have examined a large number of hydrocarbons containing methyl groups and found that in all the cases two strong band occur at 2962 and 2872 cm^{-1} corresponding to asymmetric and symmetric stretching modes of methyl group. Goel et al [47] have assigned the CH_3 asymmetric stretching modes at 3029, 2944, 2951 and 2884 cm^{-1} while symmetric stretching modes of methyl groups at 2829 and 2804 cm^{-1} in 5,6 dimethyl uracil. In view of this, the IR bands observed at 2732 and 2859 cm^{-1} with the counter part of Raman band at 2763 and 2891 cm^{-1} have been assigned as CH_3 symmetric stretching modes while the IR bands observed at 2925, 2976 and 3012 cm^{-1} with the counter part of Raman band at 2901,2916 and 3051 cm^{-1} has been assigned as CH_3 asymmetric stretching mode in the present molecule.

The symmetrical deformation mode of hydrogen atoms of a methyl group results in an absorption band in the range 1385-1370 cm^{-1} which is extremely stable in position provides that the methyl group is attached to another carbon atom [15]. Bellamy [15] also suggested the range 1450+20 cm^{-1} for asymmetric deformation mode of methyl group. Goel et al. [47] have assigned the bands at 1518, 1500, 1475 and 1460 cm^{-1} to CH_3 asymmetric deformation modes while 1442 and 1375 cm^{-1} to CH_3 symmetric deformation modes in 4,6-dimethyl pyrimidine. In view of these assignments, the IR bands observed at 1404 and 1433 cm^{-1} have been assigned to CH_3 symmetric deformation mode while the IR band observed at 1474 cm^{-1} with the counter part of Raman band at 1485 cm^{-1}have been assigned to CH_3 asymmetric deformation modes. It also finds support from the literature [40]. For a methyl group, two rocking modes are expected. Singh et al.[40] have assigned these modes at 1030 cm^{-1} and 1050 cm^{-1} .While Ahmad et al [48] have assigned these modes at 1040 and 1065 cm^{-1}. In view of these, the IR band observed at 1050 cm^{-1} [1] with the counter part of Raman band at 1055 cm^{-1} have been assigned to this mode [29, 37, 40, 41, 48, 49]. The band observed at 232, 195 and 185 cm^{-1} have been assigned to CH_3 torsion modes in 4-amino-2-6-dimethyl pyrimidine [48]. In view of the above, the Raman bands observed at 238 cm^{-1} have been assigned to CH_3 torsional modes in 3,2,4,6-BTMA.

Thermodynamic Functions

Thermodynamic functions viz enthalpy function (H^o - E_0^0)/T, heat capacity (C_p^0), free energy -($F^0 - E_0^0$)/T , and entropy (S^0) of the compound 3,2,4,6-BTMA have been computed using the standard expressions [50,51] by taking y axis perpendicular to the molecular plane and z axis to pass through the para positions . For determining rotational contribution, the following structural parameter were used [52, 53, 54].

Bond Length	**Bond Angles**
$N_1C_1 = 1.43$	**$\angle N_1C_1C_2 = 121^\circ$**
$C_1C_2 = 1.42$	**$\angle C_1C_2C_7 = 123^\circ$**
$C_2C_3 = 1.39$	**$\angle C_7C_2C_3 = 122^\circ$**
$C_3C_4 = 1.37$	**$\angle C_2C_3B_1 = 128^\circ$**
$C_4C_5 = 1.41$	**$\angle B_1C_3C_4 = 110^\circ$**
$C_5C_6 = 1.39$	**$\angle C_3C_4C_8 = 118^\circ$**
$C_6C_1 = 1.36$	**$\angle C_8C_4C_5 = 119^\circ$**
$C_2C_7 = 1.51$	**$\angle C_5C_6C_9 = 116^\circ$**
$C_3B_1 = 1.88$	**$\angle C_9C_6C_1 = 123^\circ$**
$C_4C_8 = 1.51$	**$\angle C_1C_2C_3 = 115^\circ$**
$C_6C_9 = 1.51$	**$\angle C_2C_3C_4 = 122^\circ$**
	$\angle C_3C_4C_5 = 123^\circ$
	$\angle C_4C_5C_6 = 116^\circ$
	$\angle C_5C_6C_1 = 121^\circ$
	$\angle C_6C_1C_2 = 123^\circ$

The thermodynamic functions have been calculated at different temperatures between 200-1500 ^{O}K using 36 fundamental frequencies and assuming rigid rotor harmonic oscillator approximation. The calculation were performed for 1 mole of an ideal gas at 1 atmospheric pressure. The symmetry number for overall rotation is 2 . The principal moment of inertia were found to be 130.84 X 10^{-39}, 241.18 X 10^{-39} and 50.94 X 10^{-39} gm .cm^2 in 3,2,4,6-BTMA .While reduced moment of inertia is 3.78 X 10^{-39} cm^2 for the same molecule . The barrier height (V_O) is found to be 0.544 K cal / mol.

The variation OF enthalpy function (H° - E_0^0)/T and heat capacity (C_p^0) with absolute temperature has been shown in fig 2.4. While those of free energy function - ($F^0 - E_0^0$)/T and entropy (S^0) in the fig. 2.5. Which are also in agreement with the trend reported in literature[26, 36,55-58] .

Table- 1 Assignment of Vibrational Frequencies in (cm^{-1}) of 3, 2, 4, 6-BTMA

IR	Raman	ASSIGNMENTS
3480	3474	ν (N-H) asym
3399	3365	ν (N-H) sym.
3215	3208	ν (N-H)
3012	3051	ν (C-H), ν CH_3 asym
2976	2916	ν (C-H), ν CH_3 asym
2925	2901	ν CH_3 asym
2859	2891	ν CH_3 sym
2732	2763	ν CH_3 sym
1723	1715	β (N-H)
1622	1630	NH_2 scissoring
1545	1550	ν (C-C), ν asym(C-NO_2)
1528	1535	ν (C-C)
1474	1485	CH_3 asym. Def.
1449	-	CH_3 asym. Def.
1433	-	CH_3 sym. Def.
1404	-	CH_3 sym. Def.
1387	-	ν (C-C), ν sym(C-NO_2)
1316	1349	ν (C-C), ν (C-CH_3)
1296	1301	ν (C-NH_2)
1263	-	ν (C-NH_2)
1196	1205	ν C-CH_3
1147	1155	β (C-H)
1050	1055	CH_3 Rocking
1014	1045	NH_2 Twisting
980	1010	γ (C-C-C) Trigonal bending
922	955	γ (C-H)
868	905	γ (C-H)
802	800	C-C Ring breathing
750	-	ν (C-Br)
731	755	γ (C-C), NO_2 Wagging
-	673	NH_2 Wagging
574	565	β (C-C)
549	-	NO_2 Rocking
516	-	NO_2 Rocking
466	465	ν (C-Br)
427	435	γ (C-C), NH_2 Torsion

	365	β ($C-CH_3$)
	344	β ($C-CH_3$)
	290	β (C-Br)
	251	γ ($C-CH_3$)
	238	CH_3 Torsion
	235	γ ($C-CH_3$)
	211	γ ($C-CH_3$)
	117	γ (C-Br)
	83	Lattic Vibrations
	50	Lattic Vibrations

Where

ν -Stretching
γ - Out-of-plane bending
asym. - Asymmetric
β - In-plane bending
sym. - Symmetric
def. - Deformation

Table- 2 Thermodynamic Functions of 3, 2, 4, 6-BTMA (Cal./Mole-K)

TEMPERATURE (K)	**-(F°- E_0^0)/T**	**S°**
200	59.29	21.47
300	65.28	29.12
400	70.71	35.66
500	75.75	41.20
600	80.48	45.79
700	84.96	49.59
800	89.20	52.75
900	93.23	55.39
1000	97.07	57.61
1100	100.74	59.49
1200	104.25	61.08
1300	107.61	62.44
1400	110.83	63.61
1500	113.93	64.61

Where S° = entropy, F° = free energy, and E_0^0 = zero point energy

Table- 3 Thermodynamic Functions of 3, 2, 4, 6-BTMA (Cal./Mole-K)

TEMPERATURE (K)	$(H^o - E_0^0)/T$	C_p^0
200	12.78	21.47
300	16.99	29.12
400	20.80	35.66
500	24.40	41.20
600	27.59	45.79
700	30.47	49.59
800	33.06	52.75
900	35.40	55.39
1000	37.51	57.61
1100	39.43	59.49
1200	41.17	61.08
1300	42.75	62.44
1400	44.20	63.61
1500	45.53	64.61

Where $(H^o - E_0^0)$ - Enthalpy, C_p^0 - Heat Capacity

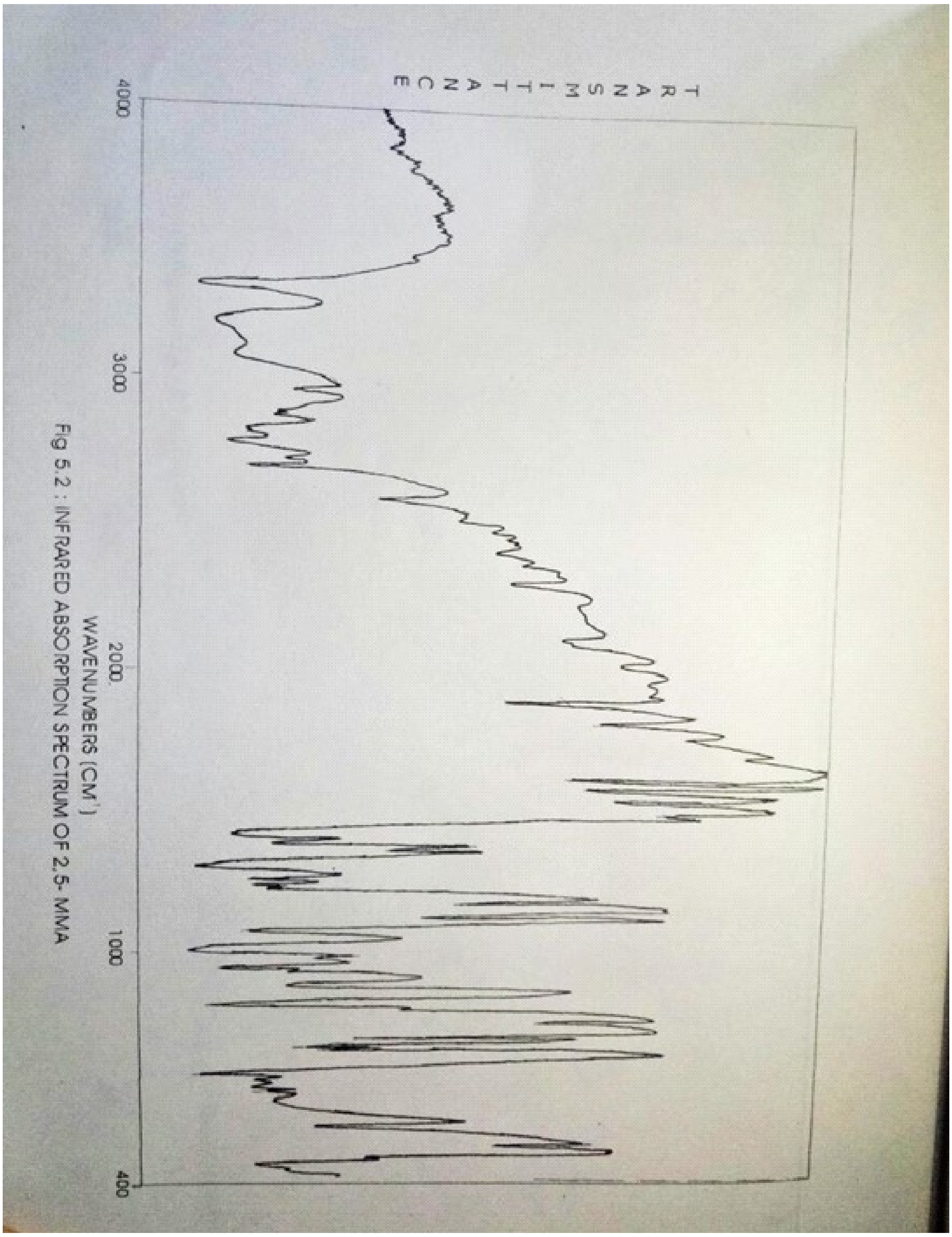


Fig 5.2 : INFRARED ABSORPTION SPECTRUM OF 2,5- MMA

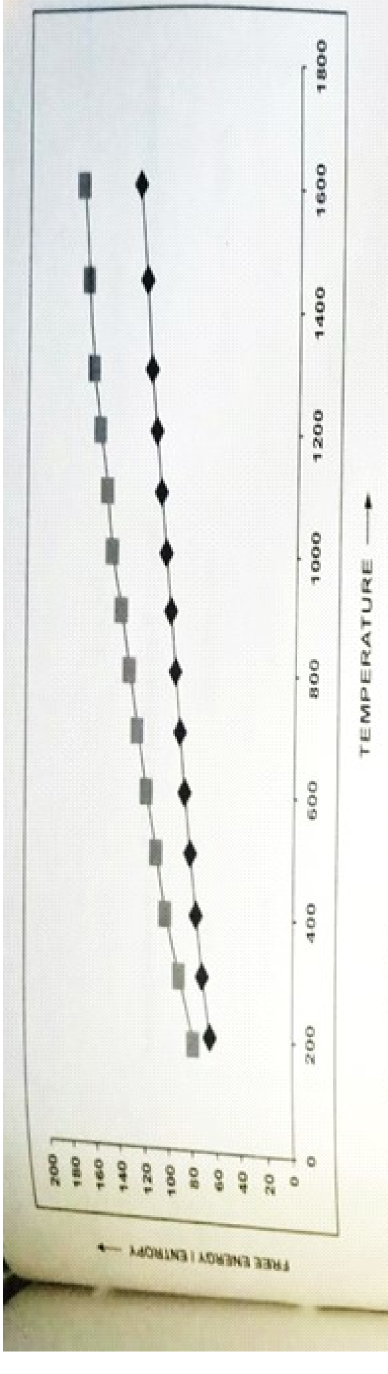


Fig. 5.4 Temperature Vs Free Energy / Entropy of 2,5-MMA

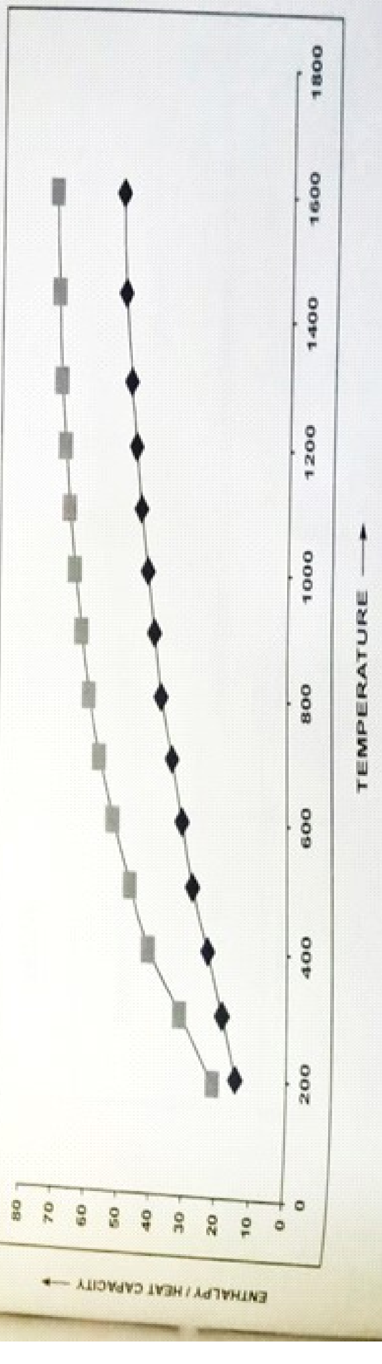


Fig. 5.5 Temperature Vs Enthalpy / Heat Capacity of 2,5-MMA

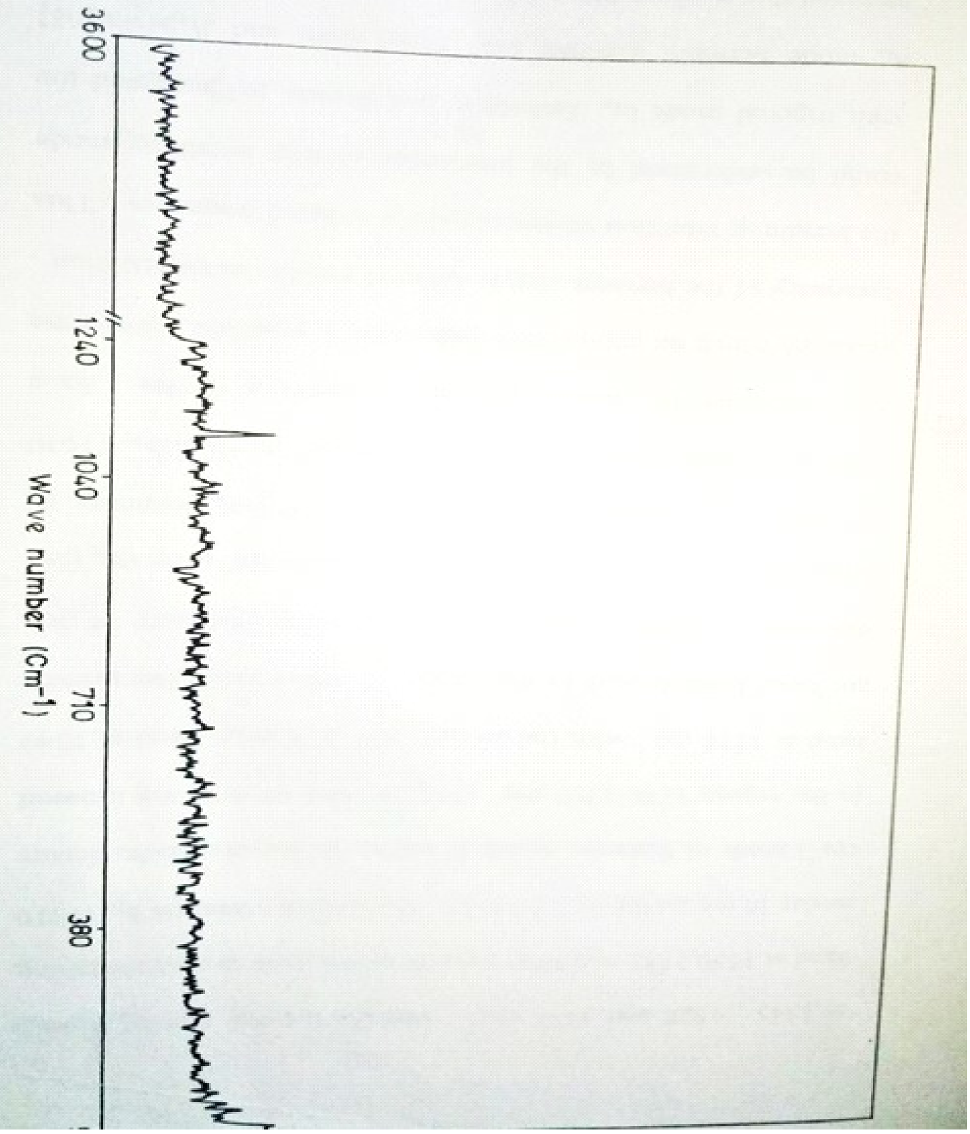


Fig.5.3: Laser Raman Spectrum of 2-Methoxy-5-Methyl Aniline.

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