

Infrared and Raman spectra of vicinally trisubstituted 2-methyl, 3-chloroaniline and 2-methyl, 6-chloroaniline

A R SHUKLA¹, C M PATHAK*, N G DONGRE², B P ASTHANA and JACOB SHAMIR[†]

Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221 005, India

[†]Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

¹Present address: Department of Non-Conventional Energy Sources, Block No. 14, CGO Complex, New Delhi 110 003, India

²Department of Physics, Harish Chandra Post-graduate College, Varanasi 221 001, India

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Abstract. The IR and Raman spectra of 2-methyl, 3-chloroaniline (2-M, 3-CA) and 2-methyl, 6-chloroaniline (2-M, 6-CA) have been recorded at room temperature in the region 3600-100 cm⁻¹. A vibrational analysis has been made using additional frequencies obtained from IR studies at 223 and 123 K and also including the polarization measurement of the Raman lines. A comparative study of these two molecules together with the spectra of 2,3-dimethylaniline (2,3-DMA), investigated earlier, has been presented. The anomalous behaviour of certain normal modes at low temperatures indicates the presence of an intermolecular hydrogen bonding of the N-H...N type in 2-M, 3-CA and 2,3-DMA, whereas, in 2-M, 6-CA, an intramolecular hydrogen bonding of the type N-H...Cl has been detected owing to the presence of the highly electronegative Cl atom at the ortho position.

Keywords. Infrared and Raman spectra; normal modes; spectral changes; hydrogen bonding, inter-and intra-molecular; phase transition.

1. Introduction

The near IR spectra of 2-M, 3-CA and 2-M, 6-CA were first investigated by Sharma and Dwivedi (1976) who have reported the frequency assignments of 35 and 37 normal modes in the respective molecules out of a possible 45 normal modes in each molecule. Our recent study on 2,3-DMA (Shukla *et al* 1986), and earlier studies on substituted benzenes (Varsanyi 1974) have revealed that more fundamentals can be observed if the spectra are recorded at low temperatures. In an attempt to investigate the influence of the three vicinal substitutions in benzene on the normal modes of the benzene frame, a comparative study of the normal modes of the molecules under investigation has been presented, along with those of 2,3-DMA (Shukla *et al* 1986). The investigation of the low temperature spectra has led to observation of many new fundamental frequencies. With the help of frequencies observed and analysed, it has been possible to propose frequency assignments for all the 45 normal modes in each molecule under discussion. The solution spectra as well as the low temperature spectra have further given strong evidence that both

* To whom all correspondence should be addressed.

the molecules are involved in one or the other kind (intermolecular or intramolecular) of hydrogen bonding as expected.

2. Experimental

The samples of 2-M, 3-CA and 2-M, 6-CA, both liquids at room temperature (b.p. 225°C), were obtained from Koch-Light, England. The reported purity was better than 98.5% in both the samples. The samples were redistilled several times under reduced pressure before use. The experimental details of recording the near IR, far IR and Raman spectra at room temperature, and IR spectra at 223 and 123 K, using a variable temperature cell, have been described elsewhere (Shukla *et al* 1986). The IR and Raman spectra of 2-M, 3-CA only has been reproduced in figure 1 covering the spectral region 3600–100 cm^{-1} . The observed spectral features in 2-M, 3-CA are compared with those of 2,3-DMA (Shukla *et al* 1986), wherever necessary. The accuracy of measurement was nearly $\pm 2 \text{ cm}^{-1}$ to $\pm 5 \text{ cm}^{-1}$. The frequencies of the normal modes of the benzene frame and their assignments, in Wilson's notation (1934), have been collected for the above three molecules in table 1. The observed

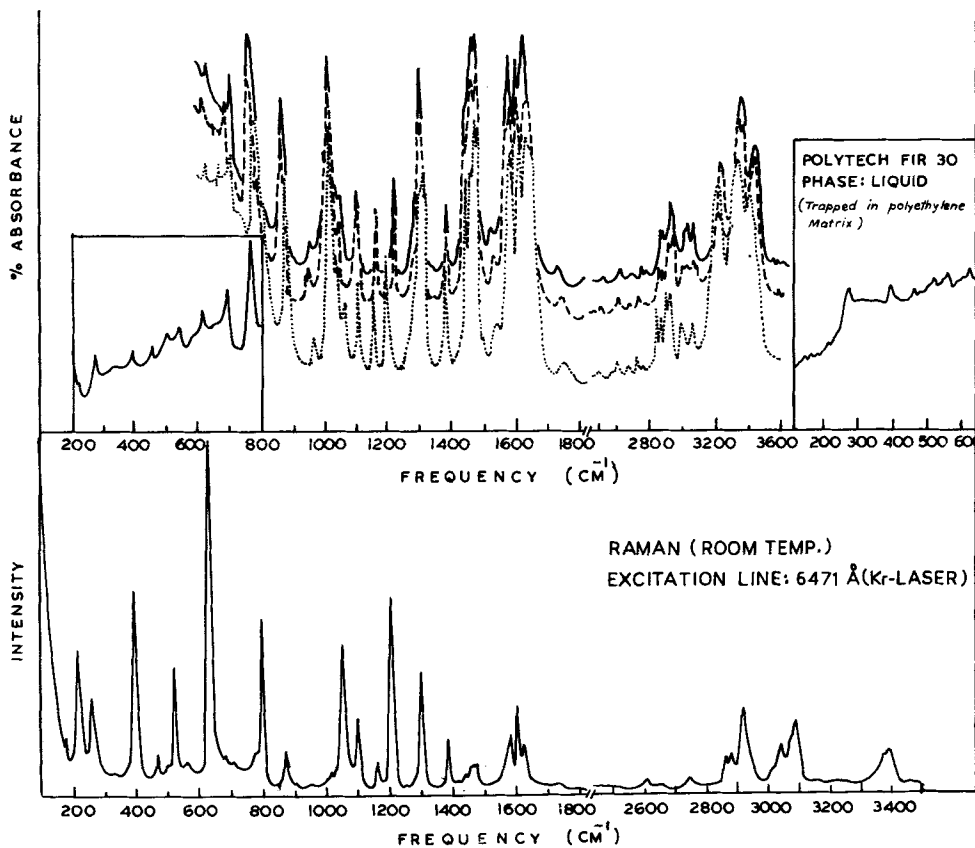


Figure 1. IR and Raman spectra of 2-methyl, 3-chloroaniline (thickness – 12 μ ; — IR at room temperature; - - - - IR at 223 K; IR at 123 K).

Table 1. Comparison of the frequencies[@] of ring modes (cm⁻¹) in 2M, 3-CA, 2M, 6-CA and 2,3-DMA.

Designation of mode (a)	Description of mode (b)	Present work			
		2M, 3-CA	2M, 6-CA	2, 3-DMA ^c	
<i>Species a'</i>					
ν_1	2	ν_{C-H}	3084* IR, <i>mw</i>		3070 IR, <i>m</i>
			3085 R, <i>m, p</i>	3080 R, <i>ms, p</i>	3075 R, <i>m, p</i>
ν_2	20b	ν_{C-H}	3064 IR, <i>mw</i>	3069 IR, <i>m</i>	3023 IR, <i>ms</i> (ν_3)
			3070 R, <i>sh, p</i>	3069 R, <i>sh, p</i>	—
ν_3	7a	ν_{C-H}	3028 IR, <i>mw</i>	3025 IR, <i>m</i>	3040 IR, <i>ms</i> (ν_2)
			3038 R, <i>m, p</i>	3031 R, <i>m, p</i>	3044 R, <i>ms, p</i>
ν_4	8b	ν_{C-C}	1599 IR, <i>s</i>	1591 IR, <i>s</i>	1599* IR, <i>vs</i>
			1599 R, <i>m, dp</i>	1595 R, <i>w, dp</i>	1596 R, <i>s, p</i>
ν_5	8a	ν_{C-C}	1577 IR, <i>s</i>	1574 IR, <i>s</i>	1574 IR, <i>sh</i>
			1578 R, <i>m, p</i>	1574 R, <i>ms, p</i>	1582 R, <i>sh, p</i>
ν_6	19a	ν_{C-C}	1476 IR, <i>vs</i>	1473 IR, <i>vs</i>	1472 IR, <i>vs</i> (ν_7)
			1474 R, <i>w, p</i>	1473 R, <i>ms, p</i>	1474 R, <i>w, p</i>
ν_7	19b	ν_{C-C}	1463 IR, <i>vs</i>	1468* IR, <i>vs</i>	1483 IR, <i>vs</i> (ν_6)
			1463 R, <i>w, p</i>	—	1485 R, <i>mw, dp</i>
ν_8	14	ν_{C-C}	1303* IR, <i>s</i>	1311 IR, <i>ms</i>	1308* IR, <i>sh</i>
			—	1310 R, <i>m, p</i>	1308 R, <i>sh, p</i>
ν_9	20a	ν_{C-X}	1296 IR, <i>s</i>	1285 IR, <i>ms</i>	1295 IR, <i>vs</i>
			1298 R, <i>ms, p</i>	1285 R, <i>s, p</i>	1295 R, <i>vs, p</i>
ν_{10}	3	β_{C-H}	1253* IR, <i>sh</i>	1250 IR, <i>ms</i>	1260 IR, <i>ms</i>
			1252 R, <i>vw</i>	1250 R, <i>w, p</i>	1260 R, <i>s, p</i>
ν_{11}	13	ν_{C-X}	1213 IR, <i>m</i>	1195 IR, <i>mw</i>	1200 IR, <i>mw</i>
			1202 R, <i>s, p</i>	1195 R, <i>ms, p</i>	1200 R, <i>s, p</i>
ν_{12}	9b	β_{C-H}	1158 IR, <i>m</i>	1150 IR, <i>w</i>	1166 IR, <i>m</i>
			1168 R, <i>mw, dp</i>	1150 R, <i>mw, dp</i>	1168 R, <i>m, dp</i>
ν_{13}	18a	β_{C-H}	1101 IR, <i>m</i>	1102* IR, <i>sh</i>	1094 IR, <i>vs</i> (ν_{14})
			1100 R, <i>m, p</i>	1099 R, <i>sh, p</i>	1094 R, <i>s, p</i>
ν_{14}	6b	ϕ_{C-C-C}	867 IR, <i>s</i>	849 IR, <i>ms</i>	542 IR, <i>mw</i> (ν_{17})
			867 R, <i>m, p</i>	848 R, <i>w, p</i>	540 R, <i>s, p</i>
ν_{15}	12	ϕ_{C-C-C}	799 IR, <i>ms</i>	828 IR, <i>m</i>	821 IR, <i>s</i>
			799 R, <i>s, p</i>	825 R, <i>s, p</i>	814 R, <i>vw</i>
ν_{16}	1	Ring breath	631 IR, <i>s</i>	632 IR, <i>s</i>	662 IR, <i>s</i>
			632 R, <i>vvs, p</i>	633 R, <i>vvs, p</i>	667 R, <i>vvs, p</i>
ν_{17}	6a	ϕ_{C-C-C}	524 IR, <i>ms</i>	527 IR, <i>w</i>	490 IR, <i>m</i> (ν_{18})
			523 R, <i>ms, p</i>	528 R, <i>m, p?</i>	490 R, <i>s, dp</i>
ν_{18}	18b	β_{C-X}	468 IR, <i>m</i>	471 IR, <i>m</i>	472 IR, <i>m</i> (ν_{19})
			469 R, <i>mw, p</i>	469 R, <i>ms, p</i>	473 R, <i>vw, dp</i>
ν_{19}	7b	ν_{C-X}	399 IR, <i>ms</i>	390 IR, <i>m</i>	1128 IR, <i>m</i> (ν_{13})
			399 R, <i>s, p</i>	390 R, <i>s, p</i>	1120 R, <i>w, p</i>
ν_{20}	9a	β_{C-X}	326 IR, <i>wb</i>	329 IR, <i>vw</i>	335 IR, <i>wb</i>
			330 R, <i>vw</i>	329 R, <i>w, p</i>	330 R, <i>mw, p</i>
ν_{21}	15	β_{C-X}	277 IR, <i>m</i>	281 IR, <i>ms</i>	279 IR, <i>m</i>
			273 R, <i>sh</i>	282 R, <i>mw, p</i>	280 R, <i>m, p</i>

Table 1. (Continued)

Designation of mode (a)	Description of mode (b)	Present work			
		2M,3-CA	2M,6-CA	2,3-DMA ^c	
<i>Species a''</i>					
ν_{22}	5	γ_{C-H}	957 IR, <i>mw</i>	950 IR, <i>w</i>	952 IR, <i>mw</i>
			958 R, <i>vw</i>	952 R, <i>vw</i>	—
ν_{23}	17a	γ_{C-H}	904 IR, <i>vw</i>	895 IR, <i>w</i>	898 IR, <i>mw</i>
			903 R, <i>vw</i>	896 R, <i>vw</i>	899 R, <i>vw</i>
ν_{24}	11	γ_{C-H}	772 IR, <i>vs</i>	760 IR, <i>s</i>	773 IR, <i>vs</i>
			772 R, <i>sh, dp</i>	765 R, <i>vw</i>	773 R, <i>vw</i>
ν_{25}	4	δ_{C-C-C}	704 IR, <i>s</i>	723 IR, <i>s</i>	713 IR, <i>vs</i>
			708 R, <i>w, dp</i>	—	715 R, <i>vw</i>
ν_{26}	16b	δ_{C-C-C}	561 IR, <i>ms</i>	538 IR, <i>ms</i>	555 IR, <i>ms</i>
			561 R, <i>w, dp</i>	542 R, <i>w, dp</i>	557 R, <i>w, dp</i>
ν_{27}	16a	δ_{C-C-C}	—	—	505 IR, <i>mw</i>
			498 R, <i>w, dp</i>	502 R, <i>w, dp</i>	512 R, <i>vw, dp</i>
ν_{28}	10b	γ_{C-X}	—	250 IR, <i>w</i>	258 IR, <i>w</i>
			261 R, <i>ms, dp</i>	245 R, <i>ms, dp</i>	—
ν_{29}	10a	γ_{C-X}	221 IR, <i>w</i>	228 IR, <i>w</i>	235 IR, <i>w</i>
			221 R, <i>s, dp</i>	228 R, <i>ms, dp</i>	235 R, <i>s, dp</i>
ν_{30}	17b	γ_{C-X}	143 IR, <i>vw</i>	140 IR, <i>w</i>	145 IR, <i>vw</i>
			—	145 R, <i>w, dp</i>	145 R, <i>vw</i>

^a Mulliken's notation (1955); ^b Wilson's notation (1934); ^c Shukla et al (1986); The assignment of the modes in Wilson's (1934) notation remains the same for all the three molecules, but in Mulliken's (1955) notation they differ at certain places in the case of 2,3-DMA and these are given in parenthesis against the corresponding frequencies.

* Observed at 223 and 123 K; ** Observed at 123 K; # Observed at 223 K; IR, infrared; R, Raman; *p*, polarized; *dp*, depolarized; *b*, broad; *s*, strong; *m*, medium; *w*, weak; *ms*, medium strong; *mw*, medium weak; *vw*, very weak; *vs*, very strong; *vvs*, very very strong; *vw*, very very weak; *sh*, shoulder.

frequencies of the normal modes associated with the substituent groups in the above three molecules have been collected separately in table 2.

3. Comparative study of the various ring modes

For the sake of comparison of the various ring modes in the two molecules under investigation, with those of 2,3-DMA (Shukla et al 1986), all the normal frequencies are collected together in table 1.

3.1 C-H stretches

The three C-H stretches in a vicinally trisubstituted benzene correspond to the modes 2, 20b and 7a (table 1). All the three frequencies have been observed in the present work for both the molecules with the spectra recorded at 223 K giving the best results. One would expect the spectral features in 2-M, 3-CA and 2-M, 6-CA to be similar to those of 2,3-DMA. The observed bands corresponding to the three

Table 2. Comparison of group frequencies^a (cm⁻¹) in 2M, 3-CA, 2M, 6-CA and 2,3-DMA.

Designation of mode	Description of mode	Present work		
		2M,3-CA	2M,6-CA	2,3-DMA ^c
<i>NH₂ group:</i>				
ν_{as}	(NH) _{as} ^{str}	3472 IR, <i>ms</i>	3480 IR, <i>s</i>	3449 IR, <i>s</i>
		3470 R, <i>w, dp</i>	3479 R, <i>w</i>	—
ν_{sy}	(NH) _{sy} ^{str}	3385 IR, <i>s</i>	3389 IR, <i>s</i>	3367 IR, <i>vs</i>
		3385 R, <i>mb, p</i>	3390 R, <i>b, p</i>	3370 R, <i>m, p</i>
β_{sy}	(NH ₂) _{sy} ^{def}	1622 IR, <i>vs</i>	1617 IR, <i>vs</i>	1621 IR, <i>vs</i>
		1622 R, <i>mw, p</i>	1617 R, <i>s, p</i>	1621 R, <i>m, p</i>
β_{as}	(NH ₂) ^{twist}	1045 IR, <i>m</i>	1079 IR, <i>s</i>	1045 IR, <i>m</i>
		1048 R, <i>s, p</i>	1080 R, <i>s, p</i>	1045 R, <i>s, p</i>
γ_{sy}	(NH ₂) ^{o.p.wag}	610 IR, <i>mv</i>	590 IR, <i>wb</i>	626 IR, <i>s</i>
		608 R, <i>w, sh</i>	585 R, <i>wb</i>	630 R, <i>vvw</i>
τ'	(NH ₂) ^{tors}	284 IR, <i>sh</i>	293 IR, <i>vw</i>	274 IR, <i>sh</i>
		—	298 R, <i>vw</i>	—
<i>CH₃ group(s)</i>				
ν_{as}	(CH) _{as} ^{str}	—	—	—
		—	—	2978 R, <i>w, p</i>
ν_{as}	(CH) _{as} ^{str}	—	2975 IR, <i>m</i>	2967 IR, <i>s</i>
		2965 R, <i>w</i>	2980 R, <i>w, p</i>	—
ν_{as}	(CH) _{as} ^{str}	2935 IR, <i>m</i>	2933 IR, <i>ms</i>	2941 IR, <i>s</i>
		2937 R, <i>sh, p</i>	2934 R, <i>w</i>	—
ν_{sy}	(CH) _{sy} ^{str}	2916 IR, <i>m</i>	2916 IR, <i>ms</i>	2923 IR, <i>s</i>
		2918 R, <i>ms, p</i>	2919 R, <i>ms, p</i>	2923 R, <i>s, p</i>
ν_{sy}	(CH) _{sy} ^{str}	—	—	2904* IR, <i>s</i>
		—	—	2910 R, <i>s, p</i>
δ_{as}^+	(CH ₃) _{as} ^{def}	—	—	—
		—	—	1462 R, <i>s, h</i>
δ_{as}^+	(CH ₃) _{as} ^{def}	1450** IR, <i>s</i>	1442 IR, <i>s</i>	1455** IR, <i>sh</i>
		1450 R, <i>w</i>	1445 R, <i>m, dp</i>	1450 R, <i>mw</i>
δ_{as}^+	(CH ₃) _{as} ^{def}	—	—	1444 IR, <i>s</i>
		—	—	1443 R, <i>mw</i>
δ_{as}^+	(CH ₃) _{as} ^{def}	1438 IR, <i>s</i>	1437 IR, <i>s</i>	1437* IR, <i>s</i>
		1438 R, <i>w, p</i>	1437 R, <i>m, p</i>	1438 R, <i>mw</i>
δ_{sy}	(CH ₃) _{sy} ^{def}	1380 IR, <i>m</i>	1378 IR, <i>m</i>	1383 IR, <i>ms</i>
		1380 R, <i>mw, p</i>	1379 R, <i>m, p</i>	1383 R, <i>s, p</i>
δ_{sy}	(CH ₃) _{sy} ^{def}	—	—	1376* IR, <i>w</i>
		—	—	1376 R, <i>sh, p</i>
δ_{as}^-	(CH ₃) ^{rock}	1028* IR, <i>m</i>	1033 IR, <i>m</i>	1043* IR, <i>m</i>
		1023 R, <i>vw, p</i>	1035 R, <i>mw, p</i>	—
δ_{as}^-	(CH ₃) ^{rock}	1011 IR, <i>vs</i>	994 IR, <i>m</i>	1018 IR, <i>m</i>
		1012 R, <i>vw, p</i>	997 R, <i>m, p</i>	1021 R, <i>w, p</i>
δ_{as}^-	(CH ₃) ^{rock}	—	—	991 IR, <i>ms</i>
		—	—	991 R, <i>s, p</i>
δ_{as}^-	(CH ₃) ^{rock}	—	—	871 IR, <i>ms</i>
		—	—	—
τ	(CH ₃) ^{tors.}	188 IR, <i>w</i>	185 IR, <i>w</i>	185 IR, <i>w</i>
		181 R, <i>w</i>	182 R, <i>w</i>	184 R, <i>vw</i>

as = asymmetric, *sy* = symmetric, *def* = deformation, *str.* = stretch; *tors* = torsion; *o.p.* = out of plane; for other abbreviations see table 1 footnote.

C-H stretching in 2-M, 3-CA and 2-M, 6-CA have intensities lower than the intensities of the corresponding modes in 2,3-DMA. This change in intensity has been attributed to the presence of an electronegative atom Cl, in both the methyl chloroanilines, which changes the polarity (Wexler 1967) from C^+-H^- to C^-H^+ .

3.2 C-C stretches

The various C-C stretches, in Wilson's (1934) notation, correspond to the modes 8a, 8b, 14, 19a and 19b (table 1). The frequency of mode 14 is usually insensitive to any type of substituent (Varsanyi 1974) and its frequency has been found to be fairly constant in the present study also. It may be noted that the IR band corresponding to this mode 14 overlapped with the C-NH₂ stretch in the case of 2-M, 3-CA, similar to that observed in 2,3-DMA (Shukla *et al* 1986), in the room temperature IR spectra, but the two modes got well separated in the spectra recorded at low temperatures.

The next two C-C stretching modes, 8a and 8b have been distinctly observed and assigned in both the molecules. It is obvious from table 1 that the frequencies of this pair of vibrations (8a and 8b) are fairly insensitive to the nature and position of the substituents in the case of all the three vicinally trisubstituted benzenes. The high degree of depolarization of the mode 8b in the Raman spectra, as measured in the present study, is more or less a characteristic property of this mode and has been found in a large number of molecules (Herz 1941). The other pair of C-C stretching modes, 19a and 19b appears characteristically with good intensity and the frequency of mode 19b gets affected by the nature of the substituents, whereas the frequency of mode 19a remains almost unaffected.

3.3 C-H in-plane bends

The three C-H in-plane bends in 2-M, 3-CA and 2-M, 6-CA correspond to modes 3, 9b and 18a. The frequency of mode 3 is lower, whereas the frequency of mode 18a has been found to be higher than the frequency of the corresponding modes in benzene and monosubstituted benzenes (Varsanyi 1974). It has been noticed that the intensity of mode 18a is lower in 2-M, 3-CA and 2-M, 6-CA as compared to that in 2,3-DMA (Shukla *et al* 1986). The frequency of mode 9b shows a variation in intensity which may be attributed to the nature and position of the substituent in the ring.

3.4 C-H out-of-plane waggings

The three C-H out-of-plane waggings correspond to modes 5, 11, and 17a. Modes 5 and 17a have been observed with very weak intensity, whereas, mode 11 appears with fairly good intensity. The frequency of mode 11 is, however, lowest among the three and its magnitude has been found to vary only with the relative position of the substituents, whereas the frequency of mode 5 has been found to change with the relative position as well as the nature of the substituents.

3.5 Radial skeletal vibrations

The seven radial skeletal vibrations in the molecules under investigation, correspond to modes 1, 12, 6a, 6b, 4, 16a and 16b. The radial skeletal modes 1 and

12 have been observed with good intensity in both the molecules and these two modes couple strongly with the C–X ($X = \text{light}$) stretch as a result of which, the frequencies corresponding to modes 1 and 12 assume relatively lower magnitude as compared to that observed in benzene. In the case of 2,3-DMA (Shukla *et al* 1986), the frequencies of the skeletal modes 6a and 6b both, were found to decrease as compared to that in benzene, whereas in the case of 2-M, 3-CA and 2-M, 6-CA, mode 6a behaves in a similar fashion as in 2,3-DMA (Shukla *et al* 1986), but the frequency of mode 6b increases considerably because of its coupling with the C–Cl stretching mode. Further, the frequencies of the skeletal modes 16a and 16b have been found to be higher than the corresponding frequencies in the parent molecule benzene because of their coupling with the C–X ($X = \text{substituent}$) out-of-plane wagging modes. The last skeletal mode 4 has been found to be almost insensitive to substitution in both the molecules.

3.6 C–X ($X = \text{substituent}$) stretching, bending and wagging modes

The C–X stretching vibrations in these molecules correspond to modes 7b, 13 and 20a. All the three modes, which appear at their characteristic frequencies, have been observed in the present work, and the values are listed in table 1. The C–NH₂ stretch, observed in the frequency interval 1270–1300 cm⁻¹, corresponds to mode 20a. This frequency appears with quite good intensity in the IR spectra and as a strongly polarized line with sufficiently good intensity in the Raman spectra. There seems to be a slight effect of relative position and nature of the substituents to mode 13. The relative position of the Cl atom, in methyl chloroaniline isomers investigated in this work, does not seem to affect the frequency of the C–CH₃ stretching mode 7b much, which is observed around 400 cm⁻¹ in both the molecules.

In benzene derivatives with vicinal trisubstitution (Varsanyi 1974), the in-plane C–X bends correspond to the modes 9a, 15 and 18b, and out-of-plane C–X wags correspond to the modes 10a, 10b and 17b. The frequencies of all these modes lie in the far IR region (figure 1). Only some slight influence of the substituent groups can be seen on the magnitude of the frequencies of these modes, which may be attributed to the relative position and/or the nature of the substituents.

4. Vibrations of the substituent groups and spectral changes due to hydrogen bonding

The two molecules under investigation have NH₂ and CH₃ groups as substituents. It is fairly well-known that in anilines and substituted anilines (Murthy and Rao 1968), the hydrogen atoms of the NH₂ group make an intermolecular hydrogen bond of N–H...N type and cause some spectral changes. Some special spectral features and changes were observed in 2,3-DMA (Shukla *et al* 1986). Similar spectral changes are expected in the cases of 2-M, 3-CA and 2-M, 6-CA and only some relevant points are discussed here. One finds that in the case of 2-M, 3-CA, the difference between the two values of asymmetric N–H stretching frequency, one observed in solution phase and the other in liquid phase, is nearly the same as the corresponding difference for the symmetric N–H stretching frequency. This provides evidence that the two N–H bonds behave identically in the intermolecular

hydrogen bond formation in the case of 2-M, 3-CA, almost similar to the case of 2,3-DMA (Shukla *et al* 1986). However, the behaviour of 2-M, 6-CA is quite different as regards the integrated intensities of the three bands related to the normal modes of the NH₂ group, two N–H stretches and one H–N–H bend, which actually decrease in going from liquid phase to the condensed phases. Furthermore, in 2-M, 6-CA, unlike 2-M, 3-CA the difference between the two values of the asymmetric N–H stretching frequency, one observed in solution and the other in the liquid phase, is different from the corresponding difference for the symmetric N–H stretching. It is also seen that the frequencies of the N–H stretching modes in 2-M, 6-CA do not follow the Bellamy and Williams (1957) empirical relation

$$\nu_{\text{sym}} = 345.5 + 0.876 \nu_{\text{asym}},$$

as closely as in 2-M, 3-CA or in 2,3-DMA (Shukla *et al* 1986).

The above facts suggest that in 2-M, 6-CA, the two N–H bonds do not behave in an identical fashion during the hydrogen bonding. This is most probably due to the coexistence of intramolecular hydrogen bonding along with N–H...N type intermolecular hydrogen bonding. In fact, according to Krueger (1962), the presence of an electronegative atom in the vicinity of NH₂ group in a molecule gives rise to intra-molecular hydrogen bonding and therefore it is quite likely that such hydrogen bonding of the type N–H...Cl coexists along with the intermolecular hydrogen bonding in 2-M, 6-CA.

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