Infrared and Raman spectra of 2,4-dimethylaniline

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Abstract. The infrared spectra of 2,4 dimethylaniline have been recorded in the region 3600–100 cm^{-1}. The Raman spectra with polarization measurements have been recorded and investigated for the first time in the region 3500–100 cm^{-1}. New frequency assignments have been proposed assuming the molecule to possess an approximate C_s symmetry. Fifty normal modes of the molecule, out of a possible fifty four modes, have actually been observed and assigned including twenty seven hitherto unreported frequencies. The observed spectral changes give evidence of the presence of an intermolecular hydrogen bonding of an N–H . . . N type, and suggest a solid-solid phase transition between 223 and 123 K in the molecule.

Keywords. Infrared and Raman spectra; normal modes; spectral changes; hydrogen bonding; phase transition.

1. Introduction

The infrared spectra of 2,4 dimethylaniline (hereafter referred to as 2,4-DMA) were first investigated by Prasad (1975) who has reported the frequency assignment of only 23 modes out of a possible 54. Many of his assignments are open to question. It has been difficult to observe all the fundamentals in benzene derivatives (Varsanyi 1974) but there is often a possibility of observing more fundamentals (Hainer and King 1950) if the spectra are recorded at lower temperatures.

According to Varsanyi (1974) 2,4-DMA falls under the category of 1,2,4-tri-light benzene derivatives. Although the molecule, in a strict sense, possesses the C_1 symmetry, we have proposed the assignment of the ring modes assuming an approximate C_s symmetry.

Infrared spectra have been recorded at room temperature, 223 K and 123 K along with the spectra in the solution phase choosing CS_2 as solvent. The observed frequency shifts, bandwidth changes and intensity variations give evidence of the presence of intermolecular hydrogen bonding of the N–H . . . N type and suggest a solid-solid phase transition between 223 and 123 K.

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2. Experimental

2,4 Dimethylaniline was obtained from Koch-Light, England. The reported purity of the sample was better than 98·5%. However, the liquid was redistilled several times under reduced pressure before use. The experimental details of recording the infrared spectra at room temperature, 223 K and 123 K have already been described in an earlier communication (Shukla *et al* 1986) on 2,3 dimethylaniline (2,3-DMA). The far infrared spectra in the region 600–100 cm^{-1} and the Raman spectra along with polarization measurements were recorded as described in the above communication (Shukla *et al* 1986). The slit width used in recording the Raman spectra was 2·5–5·0 cm^{-1}.

The spectra recorded at different temperatures, in different spectral ranges, have been reproduced in figures 1 to 5. Some of the weak bands marked as *vw* or *vvw*, which are actually present in the recorded spectra, may not be perceptible in the figures due to reduction in size. The accuracy of measurement was nearly ± 2 cm^{-1}.

3. Frequency assignments

The frequency assignments for the ring modes, methyl groups and the amino group have been presented under three separate heads. Wilson's (1934) numbering has been strictly followed for the assignment of ring modes. Mulliken's (1955) numbering scheme has been followed only in a restricted sense such that fundamental vibrations in each of the three categories are numbered in the decreasing order of frequency. The observed fundamental frequencies associated with the methyl groups have been labelled as $v'_1, v'_2, \ldots v'_{14}$ and those associated with the amino group have been labelled as $v''_1, v''_2, \ldots v''_6$. The frequencies of the ring modes in 2,4-DMA have been compared with the corresponding modes in similar molecules (Green *et al* 1971), 1,2,4 trimethylbenzene (1,2,4-TMB) and 4-fluoro 1,2 dimethylbenzene (4F,1,2,-DMB) in table 1.

4. Normal vibrations associated with the benzene ring

4.1 *Spectra in the region 3600–2800 cm*$^{-1}$

The liquid and solid phase (123 and 223 K) infrared spectra and the Raman spectra at room temperature recorded in this region have been reproduced in figure 1. The Raman spectrum of 2,4-DMA shows a weak line at 3078 cm^{-1} but in the infrared spectrum a weak shoulder appears at 3079 cm^{-1} only at 223 K. Although another weak shoulder is seen in the infrared spectrum at 3096 cm^{-1}, the lines at 3078 and 3079 cm^{-1} are assigned to mode number 20b and the shoulder at 3096 cm^{-1} has been explained as a combination band. The two polarized Raman lines at 3050 ($\rho = 0.44$) and 3017 cm^{-1} ($\rho = 0.30$) and their infrared counterparts at about 3045 (obscured by a strong absorption) and 3010 cm^{-1} are assigned to modes 2 and 20b respectively. However, Prasad (1975) observed a single band at 3040 cm^{-1} and assigned it to mode 7, which according to Varsanyi (1974), in a non-vicinal trisubstituted benzene, is a substituent sensitive mode having a much lower frequency. The above assignment proposed by Prasad (1975), therefore, does not seem to be justified.

Table 1. Observed frequencies (cm⁻¹) in infrared and Raman spectra of 2,4 dimethylaniline with frequency assignments.

Infrared									Raman					Assignment
Room temperature			223° K			123° K			CS₂ solution		Room temperature			
Frequency	I	$\Delta\nu_{1/2}$ cm⁻¹	Frequency	I	$\Delta\nu_{1/2}$ cm⁻¹	Frequency	I	$\Delta\nu_{1/2}$ cm⁻¹	Frequency	I	Frequency	I	Polarisation	
3441	s	102	3420	s	108	3410	s	139	3477	s	3442	vw		$\nu_{asym}(\nu_1'')$
3354	s	92	3343	s	139	3341	s	156	3391	s	3370	b	p	$\nu_{sym}(\nu_2'')$
3223	m	68	3220	s	88	3220	s	120			3230	w	p	$2 \times \nu_3''$
3126	w								3128	w				$8b + 19b$
3096	w, sh		3096	w, sh		3098	w, sh				3078	w		$8a + 19b$
			3079	w, sh										
3046	m		3042	m		3044	m		3046	sh	3050	m		$20a\ (\nu_1)$
											3017	m	p	$2(\nu_2)$
3008	s	50	3008	s	52	3011	s	49	3016	s				$20b\ (\nu_3)$
											3006	sh		$\nu_6' + \nu_5'$
2969	m	57	2966	s	61	2968	s, sh	55	2972	s	2975	w	p	$\nu_{asym}(\nu_1')$
						2936	s							$\nu_{sym}(\nu_2')$
2922	s	75	2921	s	80	2922	s	79	2923	s	2922	ms	p	$\nu_{sym}(\nu_3')$
2900	s		2897	s		2893	s		2893	w, sh				$2 \times \nu_4$
2859	ms	44	2857	s	45	2855	ms	44	2860	s	2864	m	p	$2 \times \nu_6'$
						2813	w, sh							$\nu_7' + \nu_8'$
			2790	w, sh		2789	w, sh							$7a + 19b$
2733	w	14	2733	w	14	2733	w	14			2736	mw	p	$2 \times \nu_6'$
			2697	w		2697	w							$8b + \nu_4''$
2664	w		2667	w		2667	w							$8a + \nu_4''$
2625	w		2625	w		2633	w							$8b + \nu_{11};\ 8a + \nu_{10}'$
2602	w		2605	w		2610	w							$\nu_{11} + 8a$
						2562	w							$7b + \nu_5''$
2536	w					2537	w							$8a + 17b$
						2514	w							$7a + 13$
2468	w		2468	w		2474	w							$\nu_5' + \nu_{11}$
2443	w		2446	w		2448	w							$\nu_4 + \nu_{12}'$

Table 1. *(Continued)*

Infrared											Raman			Assignment
Room temperature			223° K			123° K			CS$_2$ solution		Room temperature			
Frequency	I	$\Delta v_{1/2}$ cm^{-1}	Frequency	I	$\Delta v_{1/2}$ cm^{-1}	Frequency	I	$\Delta v_{1/2}$ cm^{-1}	Frequency	I	Frequency	I	Polarisation	
2398	w		2400	w		2400	w		2299	w				$v'_5 + 17b$
														$8a + 1$
						2136	w							$8a + 16a$
						2084	w							$v''_3 + 16b$
						2028	w							$5 + 18a$
						1973	w							$v_{10} + 7b$
1913	w		1912	w		1915	w							$v_{12} + 7b$
			1872	w		1873	w							$18a + 1$
1867	w	32	1862	w	31	1863	w	32						$v'_{12} + 5$
						1821	w							$5 + 17b$
1812	w													$5 + 7b$
1745	w	31	1751	w	32	1753	w							$11 + 17b; 2 \times 5$
1721	w		1720											$v'_{12} + 4$
											1655	w, sh		$5 + 12$
1626	s	46	1627	s	53	1629	s	73	1623	vs	1626	ms	p	$\beta_{sym}(v'_3)$
1611	s		1609	s		1609	s				1613	sh		$8b(v_4)$
1590	m		1588	ms		1586	ms, sh				1589	mw	p	$8a(v_5)$
						1548	w							$v'_{12} + 6a$
1510	vs	33	1515	vs	35	1513	vs	35			1515	mw	p	$19b(v_6)$
			1505			1506								
1493	w, sh					1498	w, sh							$3 + 15$
1463	ms	37	1464	ms	30	1465	s	24			1463	sh	dp	$\delta^+_{sym}(v'_4)$
											1458	mw		$\delta^+_{sym}(v'_5)$
1444	ms	31	1442	s	27	1442	s	24			1445	mw	dp	$\delta^+_{sym}(v_6)$
											1438	w, sh		$\delta^+_{sym}(v_7)$

ν	int (rel)	ν	int (rel)	ν	int (rel)	ν	int	ν (R)	int	dp	Assignment
1410	m (13)	1410	m (12)	1409	m (8)			1411	mw		19a (ν_7)
1379	m (11)	1379	m (12)	1380	m (14)			1381	s	p	$\delta_{asym}(\nu_8)$
								1373	w, sh		$\delta_{sym}(\nu_9)$
						1375	m	1364	w		10a + ν'_4
1313	m (9)	1315	m (10)	1318	m (12)	1320	m	1313	mw	p	14(ν_8)
1290	s (24)	1289	s (26)	1289	s (25)						3(ν_9)
1275	s (9)	1273	s (9)	1274	s (10)	1273	vs	1275	s	p	7a(ν_{10})
1240	ms (13)	1239	s (16)	1242	s (16)	1237	s	1242	m	p	13(ν_{11})
1226	mw, sh (19)	1226	mw	1229	mw						6b+4
1179	w (14)	1179	w	1180	w						4+16b
1155	ms (12)	1154	ms	1153	ms	1150	s	1155	m		18a(ν_{12})
						1122	w	1120	vw	p	18b(ν_{13})
1076	w (8)	1081	w (24)	1085	w (25)	1072	w	1076	vw		$\beta_{asym}(\nu'_4)$
1035	m (16)	1034	m (14)	1035	m (14)	1030	m	1040	w	p	$\delta_{asym}(\nu_{10})$
1012	m (15)	1013	m (10)	1013	m (10)	1008	m	1011	w	p	$\delta_{asym}(\nu_{11})$
984	mw (30)	984	mw (9)	985	mw (8)	980	mw	982	w	p	$\delta_{asym}(\nu_{12})$
						946	mw	950	w, sh		17b(ν_{22})
933	mw	933	mw (18)	934	mw (18)	930	mw	933	s	p	7b(ν_{14})
						883	m, sh				$\delta_=(\nu_{13})$
875	m	876	ms (18)	876	ms (19)	871	m	876	vw		5(ν_{23})
814	vs	817	vs (36)	821	vs (40)	812	vs	814	vw	p	11(ν_{24})
790	b, sh	787	m	790	m						10b+16a
						765	w	778	vs		12(ν_{15})
								759	sh		10a+6b
740	ms	744	ms (15)	743	s (18)	744	w				4(ν_{25})
716	ms, sh	714	ms (30)			722	m	717	vvs	p	1(ν_{16})
668	mb										I(1−3)?
590	vw							588	w, sh		$\gamma_{ny}(\nu'_5)$
562	sh							560	vs	p	6a(ν_{17})
551	s										16a(ν_{26})
482	mw							482	s	p	6b(ν_{18})
440	s							445	m	p	9b(ν_{19})
420	sh										16b(ν_{27})
379	w										I(0−2)?
											I(1−2)?

Table 1. (Continued)

Infrared									Raman					Assignment
Room temperature			223° K			123° K			CS$_2$ solution		Room temperature			
Frequency	I	$\Delta\nu_{1/2}$ cm^{-1}	Frequency	I	$\Delta\nu_{1/2}$ cm^{-1}	Frequency	I	$\Delta\nu_{1/2}$ cm^{-1}	Frequency	I	Frequency	I	Polari- sation	
341	mw										341	m	p?	9a(ν_{20})
310	w													($\nu_\tau + \nu_i$)
296	w													I(2 − 3)?
284	mw										284	m	dp	10a(ν_{28})
274	vw													$\tau'(\nu_6'')$
241	mw													10b(ν_{29})
231	w													($\nu_\tau - \nu_i$)
211	m										210	ms	p?	15(ν_{21})
185	w										184	w		$\tau(\nu_{14}$)
158	wb										155	w	dp	17a(ν_{30})

Abbreviations:

$\Delta\nu_{1/2}$: Full width at half maximum; I: intensity; p: polarized; dp: depolarized; b: broad; s: strong; m: medium; w: weak; ms: medium strong; mw: medium weak; vw: very weak; vs: very strong; sh: shoulder; vvs: very very strong.
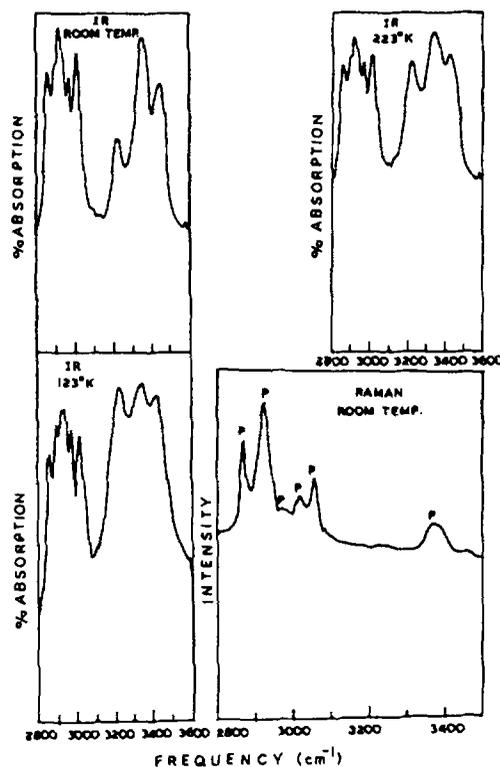
Figure 1. Infrared and Raman spectra of 2,4 dimethylaniline in the region 2800–3600 cm^{-1}.

4.2 *Spectra in the region* 1700–1100 cm^{-1}

The ring modes falling in this region are: the C–C stretching modes 8a, 8b, 19a, 19b, and 14; the C-X stretching modes 7a and 13, and the C–H in-plane bending modes 3 and 18a. Some bands are associated with normal modes of the NH_2 and CH_3 groups, whose assignments would be discussed separately.

In 2,4-DMA, like in 2,3-DMA (Shukla *et al* 1986), the frequency of the mode 8b is found to be higher than that of 8a and the frequencies of these modes for the two molecules are almost insensitive to substitution. The Raman spectrum shows a distinct, medium weak and polarized line ($\rho = 0.56$) at 1589 cm^{-1} with a shoulder at 1613 cm^{-1} while the infrared bands at 1611 and 1590 cm^{-1} are only shoulders (figure 2). The infrared spectrum further shows a very strong band at 1510 cm^{-1} and a medium weak band at 1410 cm^{-1} in the predicted (Varsanyi 1974) frequency interval for modes 19b and 19a respectively. A weakly depolarized Raman line at 1411 cm^{-1} ($\rho = 0.70$) and a polarized one at 1515 cm^{-1} ($\rho = 0.50$) are observed with equal intensity. Prasad (1975) has observed only a single band at 1510 cm^{-1} which he has assigned to mode 19.

In the 1350–1250 cm^{-1} interval, one would expect three fundamentals corresponding to modes 14, 7a and 3. In substituted benzenes containing an NH_2 group, mode number 14 has usually been observed (Varsanyi 1974) at a higher frequency than the two other modes and this fact has been supported by a normal coordinate analysis
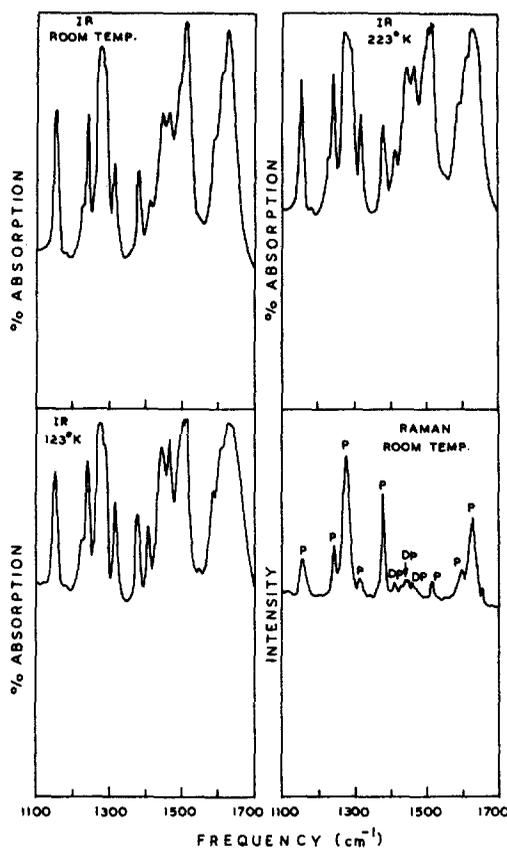
Figure 2. Infrared and Raman spectra of 2,4 dimethylaniline in the region 1100–1700 cm^{-1}.

performed by Abasbegovic *et al* (1977) for *p*-methylaniline. The frequency of mode 14 in 2,3-DMA (Shukla *et al* 1986) was found to be 1308 cm^{-1}. In the case of 2,4-DMA, an infrared band of medium intensity and a weak but strongly polarized line in the Raman spectra appeared at 1313 cm^{-1}. This frequency has been assigned to mode number 14. The C–NH$_2$ stretch has been reported to appear quite strongly in the infrared and Raman spectra of *p*-methylaniline (Abasbegovic *et al* 1977) and aniline (Evans 1960) at 1275 cm^{-1} with the Raman line being strongly polarized. In the spectra of 2,4-DMA (figure 2), a very strongly polarized and intense Raman line and a very strong infrared band have been observed at 1275 cm^{-1} and assigned to mode 7a (C–NH$_2$ stretch). Further, the infrared spectrum only shows a shoulder at 1290 cm^{-1} which has been assigned to mode 3.

In the 1250–1100 cm^{-1} interval, one would expect a C–CH$_3$ stretching mode number 13 and two C–H in-plane bending modes 18a and 18b. Although the frequency of an isolated C–X stretching mode is dependent on the mass of the linked atom (or group of atoms) and the strength of the C–X bond, the radial skeletal modes 1, 12, and 6 are known (Varsanyi 1974) to interact strongly with the C–X stretching vibration. Since two radial skeletal modes 1 and 12 have frequencies around 1000 cm^{-1} in benzene, the

C–X stretching mode in the case of light substituents will couple with modes 1 and/or 12, and as a result, its frequency increases above 1100 cm^{-1} while the frequency of mode 1 decreases below 900 cm^{-1}. This fact has been supported by normal coordinate calculations carried out on some disubstituted benzenes by Le Calve and Labarbe (1960). The observed frequencies at about 1240 cm^{-1} (figure 2) have been assigned to this mode number 13. The first bending mode 18a is assigned to the rather strong infrared and Raman bands at 1155 cm^{-1}. A weak infrared band (1122 cm^{-1}) and a very weak Raman line (1120 cm^{-1}) have been tentatively assigned to the second bending mode 18b. Prasad (1975) has reported only a single frequency at 1155 cm^{-1} and has assigned it to mode number 15, which is probably incorrect.

4.3 *Spectra in the region* 1100–600 cm^{-1}

The C–X stretching mode 7a, skeletal modes 1 and 12, out-of-plane wagging modes 17b, 5, and 11, and torsional mode 4 lie in this frequency interval. Six frequencies are reported for the first time. This region also contains bands corresponding to the normal vibrations associated with the methyl and amino groups, which will be discussed separately.

In benzene derivatives (Varsanyi 1974) some of the out-of-plane bending modes either appear with very weak intensity or do not appear at all in the infrared spectrum. Consequently, it is common practice (Green *et al* 1971; Kuwac and Machida 1978; Young *et al* 1951) to ascertain the frequency of such a mode, especially 17b, from the characteristic combination bands (Young *et al* 1951) in the region 2000–1800 cm^{-1}. However, in the case of 2,4-DMA, the solution phase infrared spectrum and the Raman spectrum (figure 3) show up a weak band around 950 cm^{-1} which has been assigned to mode 17b. The infrared band of medium intensity at 875 cm^{-1} has been assigned to mode number 5, which incidently has been observed at 871 cm^{-1} in 1,2,4-TMB (Green *et al* 1971). The frequency is significantly lower ($\approx$ 90 cm^{-1}) in 2,4-DMA than in 2,3-DMA (Shukla *et al* 1986). This change can be attributed to the relative position of the amino group with respect to the methyl groups in the two molecules. The very strong band at 814 cm^{-1} has been assigned to mode number 11.

The C–X (X = CH$_3$) stretching mode 7b in 2,4-DMA is expected at 820–1005 cm^{-1} but mode number 17b and the CH$_3$ rocking modes also fall in this region. The observed frequencies are given in table 1. The 985 cm^{-1} band was considered a suitable candidate for the CH$_3$-rock on the basis of its intensity in addition to the fact that this is a characteristic rocking frequency and has been observed at 991 cm^{-1} in 2,3-DMA (Shukla *et al* 1986). The strongly polarized Raman line at 933 cm^{-1} has a better claim for mode number 7b. If one compares this mode in 2,4-DMA with that reported (Shukla *et al* 1986) in 2,3-DMA (1128 cm^{-1}), one finds a difference of 200 cm^{-1} but similar changes have been reported in parent molecules (Green 1970), *o*-oxylene (1185 cm^{-1}) and *m*-xylene (903 cm^{-1}).

A very strong polarized Raman line at 778 cm^{-1} (figure 3) is the best candidate for mode number 12. This frequency does not appear in infrared spectra but a broad band is seen at lower temperatures at 790 cm^{-1} which is better explained as a combination band. A medium strong band observed at 740 cm^{-1} in the infrared spectra has been assigned to mode number 4. Prasad (1975) has reported a band at 735 cm^{-1} and has assigned it to mode 10 which does not seem justified as mode number 10 is actually a substituent sensitive mode (Varsanyi 1974) and is expected to be observed below
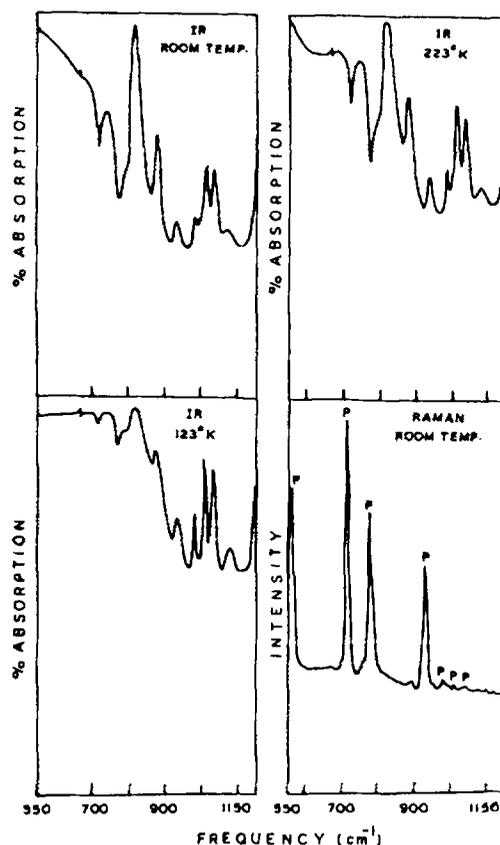
Figure 3. Infrared and Raman spectra of 2,4 dimethylaniline in the region 550–1150 cm^{-1}.

400 cm^{-1}. A very strongly polarized Raman line observed at 717 cm^{-1} and an infrared band of medium intensity at 716 cm^{-1} are assigned to mode number 1.

4.4 *Spectra in the region 600–100 cm^{-1}*

In this frequency interval, one would expect to observe the skeletal modes: 6a, 6b, 16a, and 16b; the C–X in-plane bending modes: 9a, 9b, and 15; and the C–X out-of-plane wagging modes: 10a, 10b, and 17a. In 2,4-DMA, eight frequencies have been observed for the first time.

In the spectra of 1,2,4-TMB (Green *et al* 1971), one finds that the highest frequency falling in this region corresponds to mode number 6a. Accordingly, the strong polarized Raman line at 560 cm^{-1} with its infrared partner appearing as a weak shoulder at 562 cm^{-1} (figure 5) can be assigned to mode 6a. In 1,2,4-TMB (Green *et al* 1971), a very strong band was observed in the infrared as the next lower frequency (540 cm^{-1}) which was assigned to mode 16a with its Raman partner not observed at all. In 2,4-DMA also, a similar observation is made (table 1 and figures 4 and 5) and the 551 cm^{-1} band has been assigned to mode number 16a. The next band observed at 482 cm^{-1} (IR and
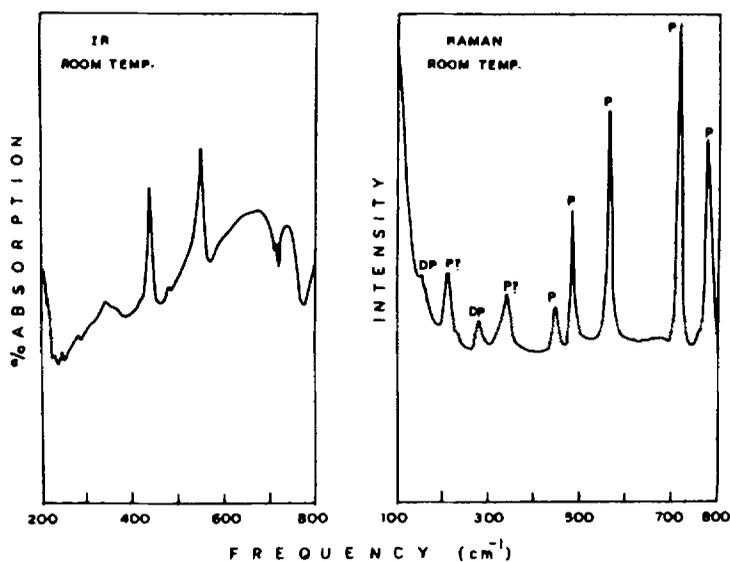
Figure 4. Infrared and Raman spectra of 2,4 dimethylaniline in the region 200–800 cm^{-1}.
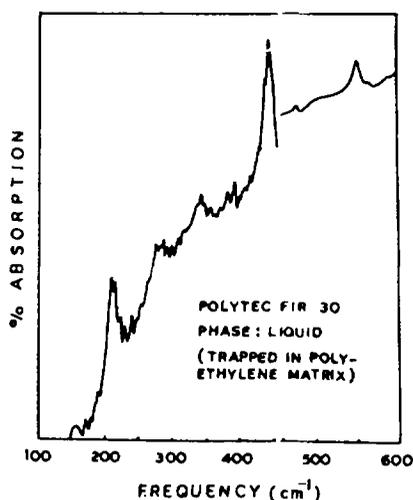
Figure 5. Infrared spectra of 2,4 dimethylaniline in the region 100–600 cm^{-1}.

Raman, $\rho = 0.30$) is assigned to mode number 6b, its frequency being quite close to those in 1,2,4-TMB and 4F,1,2-DMB (Green *et al* 1971).

In 1,2,4-TMB and 4F,1,2-DMB (Green *et al* 1971), modes 16b and 9b have been assigned to two bands quite close to each other, the first is strong in the infrared spectrum, the second is a strong polarized Raman line. Accordingly, the polarized Raman line of medium intensity observed at 445 cm^{-1} in 2,4-DMA has been assigned to mode number 9b of a' symmetry and the strong infrared band at 440 cm^{-1} has been assigned to mode number 16b of a'' symmetry.

The predicted frequency range (Varsanyi 1974) for the in-plane C–X bending mode 9a is 200–345 cm^{-1}. In 4F,1,2-DMB (Green *et al* 1971), this mode appears in the infrared and Raman spectra at 343 cm^{-1}. In 2,4-DMA, a partially polarized Raman line (ρ = 0·67) and an infrared band have been observed at 341 cm^{-1} (figures 4 and 5) and are assigned to mode 9a (a').

In the frequency interval 300–100 cm^{-1}, one would expect to observe the three C–X out-of-plane bends: 10a, 10b, and 17a in addition to a C–X in-plane bend (mode 15). The four frequencies of 2,4-DMA observed in this region have been assigned by comparison with the assignments (table 2) made for 1,2,4-TMB (Green *et al* 1971). Two of the infrared bands (figures 4 and 5), namely 211 cm^{-1} and 158 cm^{-1}, are observed in the polyethylene matrix.

5. Assignments of fundamental modes associated with substituent groups

In 2,4-DMA, a total of 24 fundamental frequencies would arise from the two methyl groups and the amino group. Eight new frequencies, five associated with the methyl groups and three with the amino group, have been observed and reported herein with appropriate assignments. All the observed fundamentals along with their assignments have been listed in table 3.

5.1 *Normal modes associated with the methyl groups*

5.1a *The stretching modes*: The infrared spectra of 2,4-DMA (figure 1) at room temperature shows a strong band at 2969 cm^{-1} (polarized Raman line at 2975 cm^{-1}) and another band at 2936 cm^{-1} recorded as a shoulder in the spectra at 123 K with its Raman partner appearing with a weak intensity. These are assigned as $\nu_{asym}(\nu'_1)$ and $\nu_{asym}(\nu'_2)$ respectively. Prasad (1975) observed only a shoulder at 2950 cm^{-1}.

The strong infrared band at 2922 cm^{-1} (figure 1) and the corresponding Raman line which is polarized, can be safely assigned to $\nu_{sym}(\nu'_3)$.

5.1b *CH_3 deformation modes*: Two strong infrared bands are seen at 1463 and 1444 cm^{-1} (figure 2, table 3) and the corresponding Raman lines are depolarized. Two more weak lines at 1458 and 1438 cm^{-1} are seen in the Raman spectrum only. We have assigned these frequencies, 1463, 1458, 1444 and 1438 cm^{-1} to the CH_3 asymmetric deformation modes δ^+_{asym} (table 3). One would expect to observe two asymmetric CH_3 deformation modes around 1375 cm^{-1} quite close to each other in accordance with the observed frequencies in 1,2,4-TMB (Green *et al* 1971). In the infrared spectra of 2,4-DMA a band of medium intensity at 1379 cm^{-1} (table 1) and the corresponding Raman line, strong and polarized (ρ = 0·30) are assigned to δ_{sym} (ν'_8). A weak shoulder observed only in the Raman spectrum at 1373 cm^{-1} has been assigned to $\delta_{sym}(\nu'_9)$.

5.1c *CH_3 rocking modes*: In 2,4-DMA, one would expect 4 rocking modes and our recorded spectra (figure 3) reveal the presence of three distinct infrared bands at 1035, 1012, and 984 cm^{-1} observed at all the temperatures. The corresponding Raman lines at 1040, 1011, and 982 cm^{-1} are weak but polarized. These frequencies are assigned to δ^-_{asym} modes (table 3). The fourth CH_3 rocking mode which appears at 871 cm^{-1} in 2,3-DMA (Shukla *et al* 1986) quite distinctly in the infrared spectrum, is neither seen in the infrared nor in the Raman spectra of 2,4-DMA. However, the bandwidth change with

Table 2. Ground state fundamental frequencies (cm^{-1}) of 2,4-dimethylaniline associated with the benzene ring in comparison with some similar molecules.

Designation of mode[a,b]	Description of mode	Expected range	1,2,4-TMB[f]	4F,1,2-DMB[f]	Present work IR	I	Raman	I	Polarization	Earlier work[d] IR	I	Assignment
Species a′												
ν_1	20a ν_{C-H}	3030–3125		3068 IR w	3079*	w	3078	vw				
ν_2	2 ν_{C-H}	3040–3100	3042 IR R w s	3058 IR w	3046	m	3050	m	p	3040	sh	7
ν_3	20b ν_{C-H}	2980–3050	3051 IR sh	3029 IR m	3008	s	3017	m	p	3020	m	7
ν_4	8b ν_{C-C}	1585–1645	1620 IR s	1624 IR s	1611	s	1613	sh		1610	m	8
ν_5	8a ν_{C-C}	1545–1605	1581 IR w	1593 IR s	1590	m	1589	mw	p	1590	sh	8
ν_6	19b ν_{C-C}	1415–1520	1507 IR vs	1506 IR s	1510	vs	1515	mw	p	1510	vs	19
ν_7	19a ν_{C-C}	1370–1455	1448 IR R w p	1416 IR m	1410	m	1411	mw	dp			
ν_8	14 ν_{C-C}	1235–1320	1348 R vw	1276 IR m	1313	m	1313	mw	p	1315	w	14
ν_9	3-β_{C-H}	1270–1310	1289 IR,R vw p	IR Rs p	1290	s						
ν_{10}	7a ν_{C-X}	1215–1320	1246 IR R vs p	1253 IR R s p	1275	s	1275	s	p	1280	s	7a
ν_{11}	13 ν_{C-X}	1090–1235	1212 IR R m p	1189 IR R s p	1240	ms	1242	m	p	1245	m	13
ν_{12}	18a β_{C-H}	1130–1175	1155 IR R s p	1151 IR R s p	1155	ms	1155	m	p	1155	m	15

Table 2. *(Continued)*

Designation of mode[a,b]	Description of mode	Expected range	1,2,4-TMB[f]	4F,1,2-DMB[f]	Present work					Earlier work[d]		
					IR	I	Raman	I	Polari-zation	IR	I	Assignment
ν_{13}	18b β_{C-H}	1065–1135	1125 IR R s p	1105 IR R s p	1122‡	w	1120	vw				
ν_{14}	7b ν_{C-X}	820–1005	925 IR R s p	947 IR R s p	933	mw	933	s	p			
ν_{15}	12 ϕ_{C-C-C}	685–800	746 IR R s p	746 IR R s p			778	vs	p			
ν_{16}	1 Ring Breath	630–740	717 IR R p	719 IR R p	716	ms	717	vvs	p			
ν_{17}	6a ϕ_{C-C-C}	440–570	555 IR R vs p	547 IR R p	562	sh	560	vs	p			
ν_{18}	6b ϕ_{C-C-C}	395–505	472 IR R s p	482 R p	482	mw	482	s	p			
ν_{19}	9b β_{C-X}	295–445	439 R p	445 R p			445	m	p			
ν_{20}	9a β_{C-X}	200–345	320 IR R s	343 IR R	341	mw	341	m	p?			
ν_{21}	15 β_{C-X}	200–290	210 R m	214 IR R	211	m	210	ms	p?			
Species a"												
ν_{22}	17b γ_{C-H}	930–990	943 IR vw	931 IR w	946‡	mw	950	sh				
ν_{23}	5 γ_{C-H}	840–915	871 IR s	860 IR s	875	m	876	vw				
ν_{24}	11 γ_{C-H}	780–855	806 IR vs	809 IR s	814	vs	814	vw				

ν_{25}	$4\,\delta_{C-C-C-C}$	675–740	705 IR s	695 IR	740 ms			735 mb	10
ν_{26}	$16a\,\delta_{C-C-C-C}$	530–620	540 IR vs	567 IR	551 s			555 s	6
ν_{27}	$16b\,\delta_{C-C-C-C}$	415–535	438 IR vs	451 IR	440 s			440 m	6
ν_{28}	$10a\,\gamma_{C-X}$	200–400	285 R w	312 IR R	284 mw	284 m	dp		
ν_{29}	$10b\,\gamma_{C-X}$	150–250	237 IR		241 mw				
ν_{30}	$17a\,\gamma_{C-X}$	100–165	146 IR R	149 R	158 w, b	155 w	dp		

[a]: Mulliken's notation (1955); [b]: Wilson's notation (1934), after Varsanyi (1974); [c]: Green et al (1971); [d]: Prasad 1975); [*]: Observed at 223 K; [†]: Observed at 123 K; [‡]Observed in CS_2 solution (for other abbreviations, see the footnote of table 1).

Table 3. Ground state fundamental frequencies (cm^{-1}) in 2,4 dimethylaniline associated with substituent groups, in comparison with some similar molecules.

Designation of mode[a,b]	Description of mode	Expected range	1,2,4-TMB[c]	4F,1,2-DMB[c]	Present work					Earlier work[d]		
					IR	I	Raman	I	Polarization	IR	I	Assignments
CH₃ group												
ν_1'	$\nu_{asym}(CH)^{Str.}_{asym}$	2960–2990	2969 IR	2974 IRRp	2969	m	2975	w	p	2950	sh	$\nu_{asym}(CH_3)$
ν_2'	$\nu_{asym}(CH)^{Str.}_{asym}$	2925–2960	2940 IR R	2947 IRRp	2936	sh				2930	mb	$\nu_{asym}(CH_3)$
ν_3'	$\nu_{sym}(CH)^{Str.}_{sym}$	2860–2935	2921 IRRp	2924 IRRp	2922	s	2922	ms	p			
ν_4'	$\delta^+_{asym}(CH_3)^{Def.}_{asym}$	1455–1470	1467 IR	1460 IR	1463	ms	1463	sh	dp	1460	mb	$\delta^+_{asym}(CH_3)$
ν_5'	$\delta^+_{asym}(CH_3)^{Def.}_{asym}$	1445–1460	1455 IR	1459 IRRdp			1458	mw				
ν_6'	$\delta^+_{asym}(CH_3)^{Def.}_{asym}$	1440–1455			1444	ms	1445	mw	dp	1440	mb	$\delta^+_{asym}(CH_3)$
ν_7'	$\delta^+_{asym}(CH_3)^{Def.}_{asym}$	1410–1445					1438	sh				
ν_8'	$\delta_{sym}(CH_3)^{Def.}_{sym}$	1330–1395	1383 IRRp	1388 IRRp	1379	m	1381	s	p	1380	w	$\delta_{sym}(CH_3)$
ν_9'	$\delta_{sym}(CH_3)^{Def.}_{sym}$	1330–1395	1377 R	1379 IRRp			1373	sh				
ν_{10}'	$\delta^-_{asym}(CH_3)Rock$	1020–1070	1038 IR	1014 IR	1035	m	1040	w	p	1040	wb	$\beta_{asym}(NH_2)$
ν_{11}'	$\delta^-_{asym}(CH_3)Rock$	1000–1025	999 IR	1005 IR	1012	m	1011	w	p	1020	m	$\delta^-_{asym}(CH_3)$
ν_{12}'	$\delta^-_{asym}(CH_3)Rock$	960–1000			984	mw	982	w	p	990	w	12
ν_{13}'	$\delta^-_{asym}(CH_3)Rock$	800–900			883*	m sh						
ν_{14}'	$\tau(CH_3)Tors.$	165–200			185	w	184	w				
NH₂ group												
ν_1''	$\nu_{as}(NH_2)^{Str.}$	3400–3500			3441	s	3442	vw		3470	mb	$\nu_{asym}(NH_2)$
ν_2''	$\nu_{sy}(NH_2)^{Str.}$	3300–3420			3354	s	3370	v		3370	mb	$\nu_{sym}(NH_2)$
ν_3''	$\beta_{sy}(NH_2)^{Def.}$	1600–1650			1626	s	1626	ms	p	1625	vs	$\beta_{sym}(NH_2)$
ν_4''	$\beta_{as}(NH_2)Twist$	1020–1130			1076	w	1076	vw	p			
ν_5''	$\gamma_{sy}(NH_2)o.p.$ wag	550–700			590	vw	588	w, sh				
ν_6''	$\tau'(NH_2)Tors.$	200–300			274	vvw						

In the column of 'Description of Modes': *asym* = asymmetric and *sym* = symmetric. For other abbreviations see the footnotes of tables 1 and 2.

temperature observed for the infrared band at 875 cm^{-1}, suggests the existence of a weak band at 883 cm^{-1} (in the infrared spectra recorded at 123 K, figure 3) which has been tentatively assigned to δ_{asym}^{-} (v'_{13}).

5.1d *CH$_3$ torsions*: Two torsional modes related to the CH$_3$ groups are expected in 2,4-DMA in the frequency interval 165–200 cm^{-1}. The infrared spectra recorded in the polyethylene matrix (figure 5) reveal the presence of a band at 185 cm^{-1} with its Raman partner appearing at 184 cm^{-1} only as a suggestion. This frequency has been assigned to $\tau(v'_{14})$. The other torsional frequency could not be observed.

5.2 *Normal modes associated with the amino group*

The infrared spectra show up two bands at 3441 and 3354 cm^{-1} (figure 1). The corresponding Raman lines are observed at 3442 and 3370 cm^{-1} (this Raman line is very broad). In any event, the infrared bands at 3441 and 3354 cm^{-1} have been assigned to $v_{asym}(v''_1)$ and $v_{sym}(v''_2)$ respectively.

In benzene derivatives (Varsanyi 1974) containing an amino group, NH$_2$ deformation β_{sym}, generally appears with good intensity. The strong Raman and infrared bands at 1626 cm^{-1}, in the case of 2,4-DMA, are then assigned to $\beta_{sym}(v''_3)$. Taking into consideration the frequencies of NH$_2$ twisting mode observed in 2,3-DMA (Shukla *et al* 1986) and *p*-toludene (Abasbegovic *et al* 1977), the weak bands observed in the spectra of 2,4-DMA (figure 2, table 3) at 1076 cm^{-1} are assigned to $\beta_{asym}(v''_4)$. The NH$_2$ wagging is expected in the frequency interval 550–700 cm^{-1} and one finds a weak band at 590 cm^{-1} in the infrared spectra taken in a polyethylene matrix and a weak Raman line at 588 cm^{-1}, both only as suggestions (figures 4 and 5). We tentatively assign these frequencies to $v_{sym}(v''_5)$.

The infrared spectrum of 2,4-DMA, recorded by trapping the molecules in a polyethylene matrix reveals the presence of three frequencies at 231, 274, and 310 cm^{-1} (figure 5). One of these frequencies probably corresponds to the NH$_2$ torsional mode which can be identified by the method of Kydd and Krueger (1978) used for benzene derivatives containing an amino group. According to these workers, if v_τ represents the frequency of the NH$_2$ torsion and v_i that of the inversion of the NH$_2$ group, the frequencies corresponding to $(v_\tau + v_i)$ and $(v_\tau - v_i)$ generally appear in the spectra. We have identified the frequency at 310 cm^{-1} as $(v_\tau + v_i)$ and at 231 cm^{-1} as $(v_\tau - v_i)$ from which one can calculate v_τ which turns out to be ≈ 271 cm^{-1}. This leads us to believe that the weak infrared band at 274 cm^{-1} most probably corresponds to $\tau'(v''_6)$.

6. Observed spectral changes due to hydrogen bonding

The presence of intermolecular or intramolecular hydrogen bonding in a molecular system is known to considerably affect (Murthy and Rao 1968) its infrared and Raman spectra. Some spectral changes have been observed by us in 2,3-DMA (Shukla *et al* 1986). Since 2,4-DMA also possesses an amino group, one can expect similar changes as one goes from CS$_2$-solution to liquid and to solid at 223 and 123 K. The spectral changes are expected to be quite significant in the N–H stretching modes, although some effects can be seen in the NH$_2$ deformation modes also. Some marked spectral changes are presented in table 4. In view of the results obtained and discussed in detail for 2,3-DMA

Table 4. Observed spectral changes in different phases of 2, 4 dimethylaniline with some calculated results giving evidence of hydrogen bonding due to the amino group.

Phase	Temperature	Observed frequency (cm⁻¹)				ν_{sym}(cal.)		Half band width (cm⁻¹)			Integrated intensity			k^c mdynes/Å corresponding to N-H stretch	Angle[c] H-N-H (degree)
		β_{sym}	ν_{asym}	$\Delta\nu$	ν_{sym}	B[a]	S[b]	β_{sym}	ν_{asym}	ν_{sym}	β_{sym}	ν_{asym}	ν_{sym}		
CS₂ Solution	Room	1623	3477	86	3391	3391	3407							6·54	111·8
$\Delta\nu$		-03	36		37										
Liquid	Room	1626	3441	87	3354	3360	3382	46	102	92	132	74	120	6·40	112·3
$\Delta\nu$		-01	21		11										
Solid	223°K	1627	3420	77	3343	3341	3352	53	108	139	121	80	105	6·34	109·8
$\Delta\nu$		-02	10		2										
Solid	123°K	1629	3410	69	3341	3333	3342	73	139	156	168	144	150	6·32	110·3

[a]Calculated value using Bellamy and Williams' relation (1957); [b]calculated value using Stewart's relation (1959); [c]calculated value using Linnett's relation (1945).

(Shukla *et al* 1986), it appears that a symmetric N–H . . . N (Shukla *et al* 1986; Bellamy and Williams 1957) type intermolecular hydrogen bonding exists in 2,4-DMA also, which slowly breaks down as the liquid is cooled down. At 123 K, the crystallization seems to be almost complete and the intermolecular hydrogen bonding assumes an asymmetric nature (Shukla *et al* 1986; Stewart 1959).

Like in 2,3-DMA (Shukla *et al* 1986), if one assumes that the interaction between the stretching and deformation modes of the NH_2 group is negligibly small and the magnitude of the force constant for the two N–H stretches, v_{sym} and v_{asym} is almost the same, one can use the relation proposed by Linnett (1945) and calculate the force constant k and the angle θ (H–N–H) in 2,4-DMA by the procedure adopted for 2,3-DMA (Shukla *et al* 1986). The results have been presented in table 4. It can be seen that the bond angle H–N–H at 223 K is 109·8° and is distinctly different from the values at room temperature and at 123 K. This indicates the anomalous behaviour of 2,4-DMA at 223 K and further suggests a phase transition of the molecule between 223 and 123 K.

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