

# FTIR and FT-Raman Spectral Investigations on 4-Aminoquinaldine and 5-Aminoquinoline

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The FTIR spectra of 4-aminoquinaldine and 5-aminoquinoline were recorded in solid phase on a Bruker IFS 66V spectrometer in the region 4000–400  $\text{cm}^{-1}$ . The FT-Raman spectra of these compounds were also recorded in the same instrument with a FRA 106 Raman module. The molecules under investigation are considered to have a  $C_S$  point group by assuming the  $-\text{NH}_2$  and  $-\text{CH}_3$  groups as point masses. All the vibrations are both IR and Raman active. The simple general valence force field (SGVFF) is adopted for both inplane and out of plane vibrations. All the frequencies are assigned in terms of fundamentals, overtones and combinations. The general agreements between the observed and calculated frequencies are satisfactory.

**Key Words:** FTIR, FT-Raman, normal coordinate analysis (NCA), potential energy distribution (PED), and simple general valence force field (SGVFF).

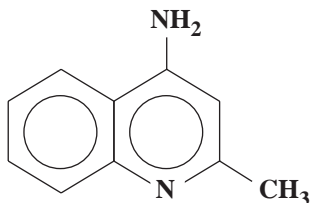
## Introduction

4-Aminoquinaldine (AMQ) (4-amino-2-methylquinoline;  $\text{C}_{10}\text{H}_{10}\text{N}_2$ ) and 5-aminoquinoline (AQ) ( $\text{C}_9\text{H}_8\text{N}_2$ ) are derivatives of quinoline and resemble naphthalene. These 2 molecules are similar in geometrical structure. It consists of 1 benzene ring and 1 pyridine ring fused together. The geometrical structure of 4-aminoquinaldine and 5-aminoquinoline are shown in Figures. 1 and 2. Quinoline is present in coal tar and bone oil. It is a biologically and pharmaceutically important molecule. Quinoline dyes are present in photographic sensitizers<sup>1</sup>. Quinoline yellow is used as textile dye for wool, nylon and silk as well as for dying paper. Printing ink contains quinoline yellow barium salt. It is also used as a colouring agent for food, drugs and in all cosmetics, except those that are used near the eyes. Quinoline yellow is soluble in spirit and hence it is widely used in lacquers, polystyrene, polycarbonates, polyamides and acrylic resins. Quinoline derivatives show promising antiphlogistic activity in rats<sup>2</sup>, are bacterial inhibitors<sup>3</sup> and are precursors to a number of antimalarial and cancer drugs<sup>4</sup>. Derivatives of aminoquinoline are used as inhibitors of the human immunodeficiency virus (HIV)<sup>5</sup>. Quinoline and isoquinoline are also active against staphylococcus, epidermis,

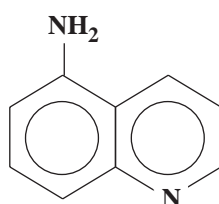
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neisseria and gonorrhoea<sup>6</sup>. The 4-Aminoquinoline nucleus of chloroquine is a drug linked to purines, adenine and guanine by a trimethylene group. Quinaldine is commonly used as an anaesthetic while handling fish. Quinoline derivatives are also used as a local anaesthetic<sup>7</sup>.



**Figure 1.** Structure of 4-aminoquinoline.



**Figure 2.** Structure of 5-aminoquinoline.

Kulkarni Jatkar<sup>8</sup> recorded the Raman spectra of  $\alpha$ - and  $\beta$ -picolines, quinoline, quinaldine and isoquinoline and also carried out preliminary studies. Picard et al.<sup>9</sup> recorded the vapour phase ultraviolet absorption spectra of quinoline and quinaldine. Samuel et al.<sup>10</sup> studied the ultraviolet absorption spectra of 7 monochloroquinolines and the 2-, 3-, 4-, 6-, 7- and 8- mono methylquinoline in 95% ethanol and 10% ethanol. The changes in intensity and the shifts in wavelength of the maxima of the monochloroquinolines were correlated with the molecular dimensions. The shifts in the wavelengths for the methylquinolines could not be associated with the dimensions of methylquinolines. Possible reasons, based on electron densities at the nitrogen atom, as influenced by the various substituents are given for the order of basis strength.

The infrared and Raman spectra of quinoline were discussed in detail by Chiorboli and Bertoluzza<sup>11</sup>. Shashidhar et al.<sup>12</sup> recorded the absorption spectra of 2-, 4-, 6- and 7-methylquinolines in vapour phase in the near ultraviolet region on a medium quartz spectrograph.

Shashidhar et al.<sup>13</sup> recorded and analysed the near ultraviolet absorption spectra of 4 methyl substituted quinolines, namely 2-, 4-, 6- and 7-methylquinolines in the vapour state. The spectra of these molecules were recorded in the region 3200-2800 Å. Shashidhar et al. also analysed the Raman and IR data of these molecules. The most intense bands at the longest wavelength side was the (0,0) band and the suggested assignments for 2-, 4-, 6- and 7-methylquinolines were given respectively. No ground state vibrations are recorded in these molecules. The spectra were analysed in association with the Raman and IR data for all these molecules. These molecules belong to  $C_S$  point group symmetry.

Robert et al.<sup>14</sup> measured spin-lattice relaxation times,  $T_1$ , of quinoline, quinaldine, isoquinoline, lepidine, 6-methylquinoline and 7-methylquinoline and of 2 quinoline related compounds having 2 nitrogen atoms in 1 fused 6 membered skeleton (quinazoline, quinoxaline) in a pure liquid form as a function of temperature using a <sup>13</sup>C NMR spectrometer. They plotted the natural log of  $T_1$  as a function of inverse temperature and found that for isoquinoline, 7-methylquinoline, quinazoline and quinoxaline there was 1 activation energy while there were 2 activation energies for quinoline, quinaldine and lepidine. For all

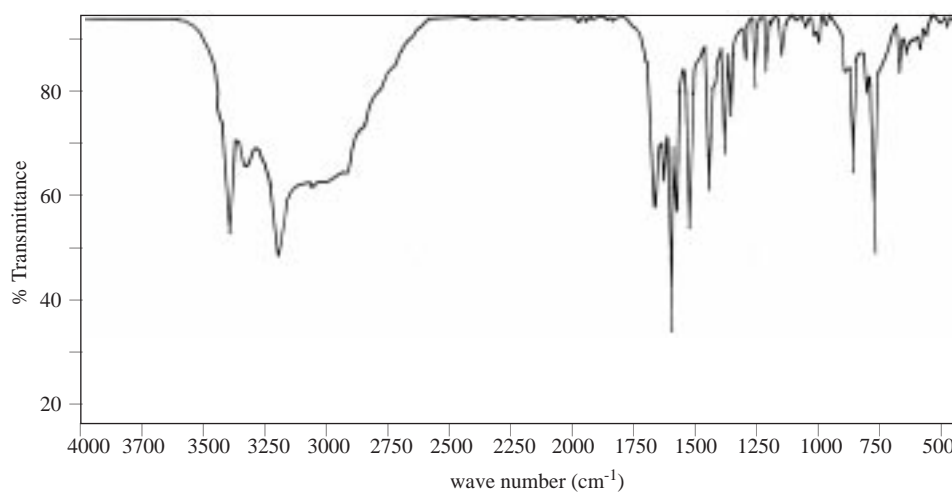
these compounds the higher temperature relaxation corresponds to an energy barrier less than 20.5 kJ mole<sup>-1</sup> and for low temperature processes an energy barrier close to 30 kJ mole<sup>-1</sup>. They have also plotted the saturated specific heat,  $C_S$ , as a function of absolute temperature for quinoline and isoquinoline. These 2 graphs were similar and suggested the existence of dynamical transition in the liquid state at a given temperature similar to super-cooled liquids.

The temperature dependence of vertically (incident) and horizontally (scattered) depolarised spectra of benzene and quinoline has been investigated by Eloutassi et al.<sup>15</sup> They also studied the anomalous effects in the temperature dependence of the depolarised Rayleigh spectra of benzene and quinoline. Hong-Cheu et al.<sup>16</sup> reported the synthesis of heterocyclic liquid crystalline molecules through fusing aromatic rings containing 3,7-disubstituted quinoline with one of the widest smectic C phases. Their naphthalene analogues are compared. The nitrogen atom in a quinoline system introduces attractive forces to aid the formation of the tilted smectic C phase, and the flexible chain length also influences the tilted smectic C phase effectively.

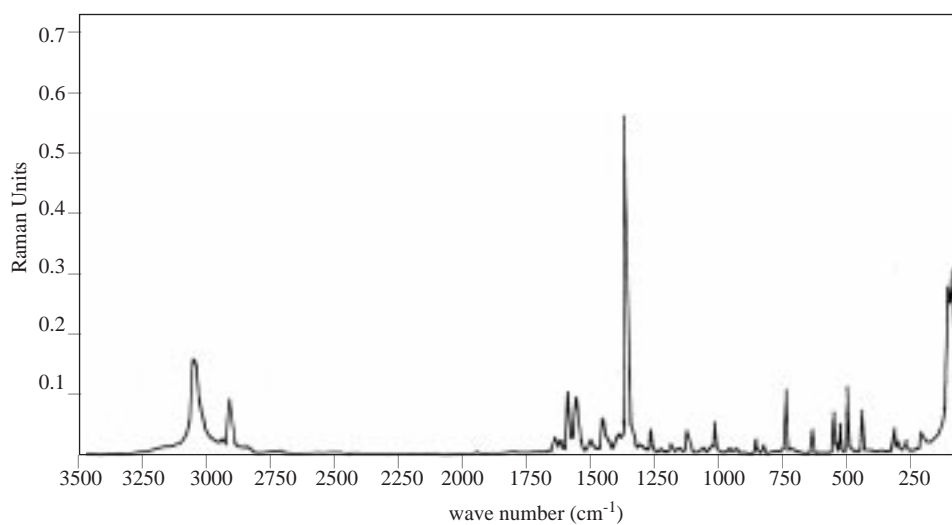
In the present investigation, the FTIR and FT-Raman spectra of 4-aminoquinoline (AMQ) and 5-aminoquinoline (AQ) are recorded and analysed to obtain complete, reliable and accurate vibrational assignments through normal coordinate analysis.

## Experimental

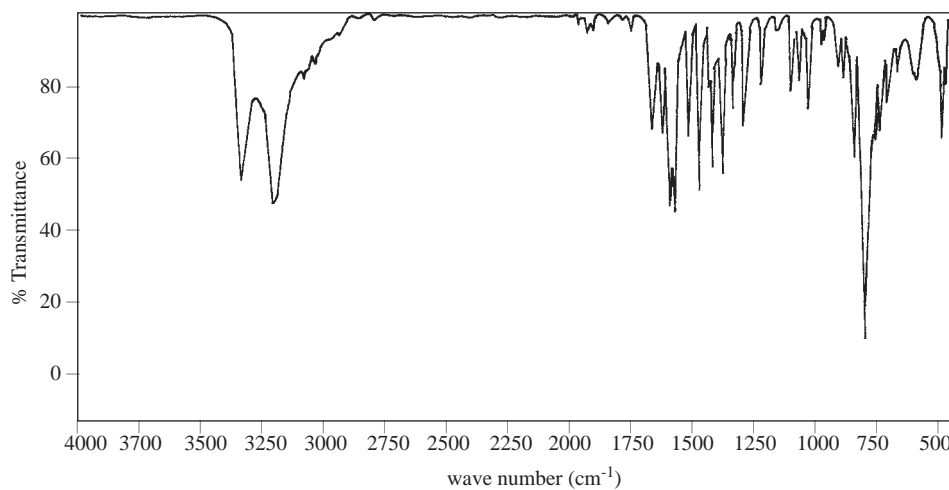
The compounds 4-aminoquinoline (AMQ) and 5-aminoquinoline (AQ) were obtained in solid form Aldrich chemicals, USA, with stated purity (AMQ 98% and AQ 97%) and used as such without further purification to record FTIR and FTR spectra. The FTIR spectra of these compounds were recorded in solid phase in the region between 4000 and 400 cm<sup>-1</sup> using a Bruker IFS 66V spectrometer, with a scanning speed of 30 cm<sup>-1</sup> min<sup>-1</sup> and a spectral width 2.0 cm<sup>-1</sup>. The frequencies for all sharp bands are accurate to  $\pm 1$  cm<sup>-1</sup>. The FT-Raman spectra were also recorded in the same instrument with a FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064  $\mu$ m line with 200 mW power and a spectral resolution of  $\pm 2$  cm<sup>-1</sup>. The FTIR and FT-Raman spectra of AMQ are shown in Figures. 3 and 4 while for AQ are given in Figures. 5 and 6.



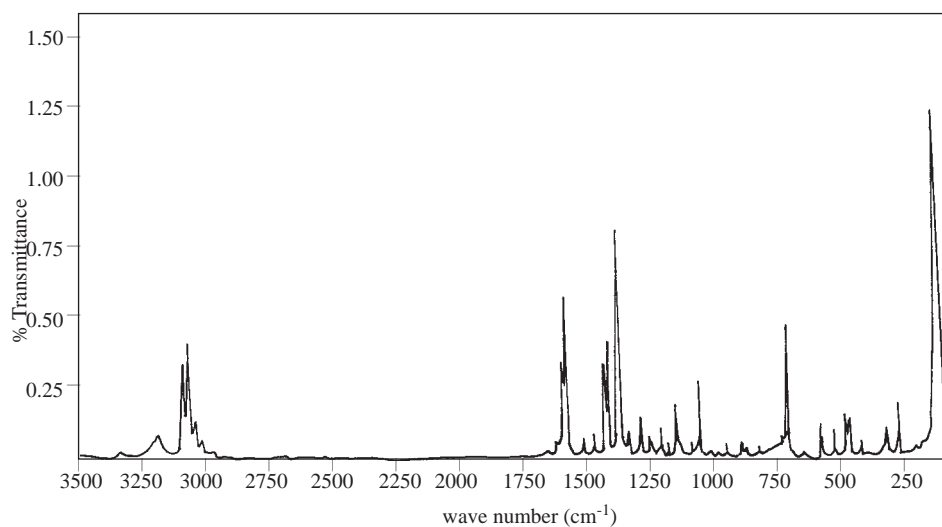
**Figure 3.** FTIR spectrum of 4-aminoquinoline.



**Figure 4.** FT-Raman spectrum of 4-aminoquinoline.



**Figure 5.** FTIR spectrum of 5-aminoquinoline.



**Figure 6.** FT-Raman spectrum of 5-aminoquinoline.

## Normal coordinate analysis

The compounds under investigation possess  $C_S$  point group symmetry by assuming  $-NH_2$  and  $-CH_3$  groups as point masses and lie in the plane of the molecule.  $C_S$  symmetry leads to 2 types of vibrations, namely  $a'$  (inplane) and  $a''$  (out of plane), that are distributed into  $\Gamma_{vib} = 43a' + 17a''$  in the case of AMQ and the 51 fundamental vibrations of AQ are distributed as  $\Gamma_{vib} = 37a' + 14a''$ . All the vibrations are active in both IR and Raman. The normal coordinate analysis program of Fuhrer et al.<sup>17</sup> was used after suitable modification to calculate vibrational frequencies and potential energy distribution (PED). This program follows the Wilson's FG matrix method<sup>18-20</sup> of vibrational analysis in which the normal coordinates are defined with respect to a set of molecular coordinates. The structural parameters necessary for the compound are taken from the Sutton table<sup>21</sup> and similar molecules. The simplified general valence force field (SGVFF) was adopted for both inplane and out of plane vibrations and the force constants were refined by the damped least square technique. The potential energy distributions are calculated using the final set of force constants. The SGVFF is shown to be very effective in normal coordinate analysis because the valence force constants can be transferred between the structurally related molecules, which is very useful in the NCA of large polyatomic molecules. A salient feature of NCA and force field calculations has been that it could reproduce the frequencies associated with the skeletal rings as well as the  $-NH_2$  and  $-CH_3$  groups within a reasonable limit ( $\pm 10 \text{ cm}^{-1}$ ) with an acceptable potential energy distribution. The common initial and final set of force constants used for both the molecules are given in Table 1.

## Results and Discussion

All the wave numbers are assigned in terms of fundamentals, overtones and combination bands. The observed wave numbers of AMQ and AQ along with their relative intensities and probable assignments, calculated wave numbers and potential energy distribution are presented in Tables 2 and 3. The wave numbers were assigned on the basis of earlier assignments on naphthalene and normal coordinate analysis by assuming  $C_S$  symmetry for these molecules.

### Carbon vibrations

In benzene, bands between  $1400$  and  $1650 \text{ cm}^{-1}$  have been assigned to C-C stretching modes. It has 2 double degenerate modes,  $1596 \text{ cm}^{-1}$  ( $e_{2g}$ ) and  $1485 \text{ cm}^{-1}$  ( $e_{1u}$ ), and 2 non-degenerate modes,  $1310 \text{ cm}^{-1}$  ( $b_{2u}$ ) and  $995 \text{ cm}^{-1}$  ( $a_{1g}$ ). In AMQ the observed stretching bands appeared at  $1344$ ,  $1371$ ,  $1415$ ,  $1438$  and  $1470 \text{ cm}^{-1}$  and in AQ the bands seen at  $1326$ ,  $1366$ ,  $1412$ ,  $1425$  and  $1465 \text{ cm}^{-1}$  have been assigned to C-C stretching vibrations. The bands occurring at  $1570$ ,  $1593$ ,  $1617$  and  $1659 \text{ cm}^{-1}$  in AMQ and  $1586$ ,  $1658$ ,  $1740$  and  $1770 \text{ cm}^{-1}$  in AQ correspond to C=C stretching modes. The band observed at  $1617 \text{ cm}^{-1}$  in AMQ is doubly assigned to C=C stretching and  $NH_2$  deformation modes.

The inplane carbon bending vibrations are obtained from the non-degenerate  $1010 \text{ cm}^{-1}$  ( $b_{1u}$ ) and  $606 \text{ cm}^{-1}$  ( $e_{2g}$ ) modes of benzene. The degenerate  $e_{2g}$  modes are observed at  $509$ ,  $538$ ,  $563$  and  $619 \text{ cm}^{-1}$  in AMQ and  $577$  and  $462 \text{ cm}^{-1}$  in AQ. Carbon out of plane bending vibrations are defined with reference to the non-degenerate  $707 \text{ cm}^{-1}$  ( $b_{2g}$ ) and degenerate  $404 \text{ cm}^{-1}$  ( $e_{2u}$ ) modes of benzene. In the present work, the carbon out of plane bending vibrations under  $C_S$  symmetry are assigned to the bands at  $449$ ,  $648$  and  $759 \text{ cm}^{-1}$  and  $478$ ,  $488$ ,  $527$ ,  $570$  and  $700 \text{ cm}^{-1}$  in AMQ and AQ respectively. The bands observed at  $648$

and  $759\text{ cm}^{-1}$  in AMQ are also doubly assigned to  $\text{NH}_2$  wagging and  $\text{CH}_3$  wagging respectively. The results are in good agreement with literature values.<sup>22,23</sup>

**Table 1.** The common initial and final set of force constants used for 4-aminoquinoline and 5-aminoquinoline (units: stretching;  $\text{mdyne.A}^{-1}$ , bending;  $\text{mdyne.A.rad}^{-2}$  and stretching-bending;  $\text{mdyne.rad}^{-1}$ ).

Types of force constants	Parameter	Coordinates involved	Initial	Final	
Diagonal constants	Stretching	$f_D$	C-H	4.500	4.489
		$f_E$	C-H	4.510	4.524
		$f_d$	C-C	2.850	2.816
		$f_e$	C-C	5.047	5.086
		$f_p$	C-N	5.224	5.281
		$f_q$	N-H	5.846	5.647
		$f_R$	N=C	10.510	9.921
Diagonal constants	Bending	$f_\alpha$	HCC	0.310	0.216
		$f_\beta$	CCC	0.543	0.358
		$f_\gamma$	CNC	0.262	0.274
		$f_\delta$	NCC	0.315	0.308
		$f_\theta$	CCN	0.315	0.198
		$f_\psi$	CCN	0.262	0.212
		$f_\xi$	HNH	0.364	0.216
Interaction constants	Stretching-Stretching	$f_{Dd}$	CH CC	0.190	0.211
		$f_{Ee}$	CH CC	0.190	0.168
		$f_{dd}$	CC CC	0.062	0.054
		$f_{de}$	CC CC	0.062	0.052
		$f_{dR}$	CC N=C	0.800	0.587
		$f_{ds}$	CC CN	0.913	0.894
		$f_{sR}$	CN N=C	0.658	0.598
		$f_{dp}$	CC CN	0.903	0.873
Interaction constants	Stretching-Bending	$f_{D\alpha}$	CH HCC	0.255	0.264
		$f_{d\alpha}$	CC HCC	0.813	0.798
		$f_{d\beta}$	CC CCC	0.360	0.362
		$f_{s\gamma}$	CN CNC	0.102	0.099
		$f_{R\delta}$	N=C NCC	0.092	0.092
		$f_{e\theta}$	CC CCN	0.486	0.474
		$f_{e\psi}$	CC HCH	0.124	0.124
		$f_{p\psi}$	CN CCN	0.121	0.119
Interaction constants	Bending-Bending	$f_{p\xi}$	CN HNH	0.044	0.044
		$f_{\alpha\alpha}$	HCC HCC	0.041	0.041
		$f_{\alpha\beta}$	HCC CCC	0.084	0.062
		$f_{\beta\beta}$	CCC CCC	0.089	0.089
		$f_{\gamma\delta}$	CNC NCC	0.107	0.091
		$f_{\gamma\theta}$	CNC CCN	0.063	0.058
		$f_{\beta\psi}$	CCC CCN	0.091	0.090

## Ring breathing

In benzene the C–C–C ring breathing ( $a_{1g}$ ) and C–C–C trigonal bending ( $b_{1u}$ ) exhibit their characteristic frequency at 995 and 1010  $\text{cm}^{-1}$  respectively. In the present study the corresponding C–C ring breathing and trigonal bending have been assigned to the bands at 783 and 1032  $\text{cm}^{-1}$  in AMQ and 827 and 1013  $\text{cm}^{-1}$  in AQ respectively. These assignments agree well with Mohan et al.<sup>24</sup>

## C–H Vibrations

The AQ molecule gives rise to 6 C–H stretching modes, whereas AMQ provides 7 C–H stretching modes, 5 from the ring and 2 from the methyl group. The aromatic structure shows the presence of C–H stretching vibrations around 3000  $\text{cm}^{-1}$ . These stretching frequencies arise from the modes of ( $a_{1g}$ ) 3062  $\text{cm}^{-1}$ , ( $e_{2g}$ ) 3047  $\text{cm}^{-1}$ , ( $b_{1u}$ ) 3060  $\text{cm}^{-1}$  and ( $e_{1u}$ ) 3080  $\text{cm}^{-1}$ . In AQ these modes are observed at 2916, 2971, 3008, 3033, 3067 and 3080  $\text{cm}^{-1}$  and in AMQ these are identified at 3060, 3037, 2783, 2722 and 2650  $\text{cm}^{-1}$ . In general, the methyl group has shown 2 characteristic C–H stretching vibrations at around 2962 and 2872  $\text{cm}^{-1}$ . In AMQ these bands are observed at 2917  $\text{cm}^{-1}$  for asymmetric stretching and 2873  $\text{cm}^{-1}$  for symmetric stretching, which are in good agreement with literature values.<sup>25</sup>

In benzene-like molecules C–H inplane bending vibrations are observed in the region 1000–1300  $\text{cm}^{-1}$  and are usually weak. The C–H out of plane bending modes of usually medium intensity arise in the region 600–900  $\text{cm}^{-1}$ .<sup>25</sup> In the present case the bands observed at 1082, 1133, 1150, 1172, 1207 and 1250  $\text{cm}^{-1}$  in AQ and 1129, 1166, 1194, 1241 and 1280  $\text{cm}^{-1}$  in AMQ are assigned to the C–H inplane bending vibrations, while 1241 and 1280  $\text{cm}^{-1}$  in AMQ are doubly assigned. The C–H out of plane bending modes for AMQ and AQ are also assigned within the said region and are presented in Tables 2 and 3.

## C=N, C–N Vibrations

The assignment of C=N and C–N stretching frequencies is a difficult task, since there are problems in identifying these frequencies from other vibrations. In AQ the medium bands at 1507 and 1281  $\text{cm}^{-1}$  are assigned to C=N and C–N stretching modes respectively. These assignments are in good agreement with earlier works.<sup>22,26</sup> In AMQ these modes are observed in IR at 1518 and 1280  $\text{cm}^{-1}$  respectively.

## CNC, NCC Bending modes

The CNC inplane bending vibration is attributed to the band observed at 325  $\text{cm}^{-1}$  in AMQ. The results of normal coordinate analysis are used to assign the CNC and CCN inplane bending vibration in AQ at 337 and 430  $\text{cm}^{-1}$  respectively. In AMQ the CCN inplane bending mode is observed in IR at 404  $\text{cm}^{-1}$ . The CNC and CCN out of plane bending modes of these molecules are presented in Tables 2 and 3.

**Table 2.** Observed and calculated wave numbers and potential energy distribution (PED) for 4-aminoquinaldine.

Species	Observed wave number		Calcd. Wave number	Assignments	% PED
	FTIR	FTR			
		91s		Lattice mode	
a''		105m	111	CNC out of plane bending	$36\eta_{CNC} + 26\eta_{CCC} + 20\eta_{CH}$
a''		220vw	231	CCN out of plane bending/ C-NH <sub>2</sub> out of plane bending	$44\eta_{CCN} + 41\eta_{C-NH_2}$
a''		280vw	296	C-CH <sub>3</sub> out of plane bending	$48\eta_{C-CH_3} + 20\eta_{CCC}$
a'		325vw	328	C-CH <sub>3</sub> inplane bending/ CNC inplane bending	$47\beta_{C-CH_3} + 41\beta_{CNC}$
a''			378*	CCC out of plane bending	
a'	404vw		410	C-NH <sub>2</sub> inplane bending/ CCN inplane bending	$39\beta_{C-NH_2} + 42\beta_{CCN} + 14\beta_{CH}$
a'	449w	450w	458	NCC inplane bending/ CCC out of plane bending	$51\beta_{NCC} + 19\beta_{CH_3} + 24\beta_{CH}$ $49\eta_{CCC} + 19\eta_{CNC} + 21\eta_{CH}$
a''		509w	511	CCC inplane bending	$56\beta_{CCC} + 21\beta_{CCN}$
a'	538vw	539vw	544	CCC inplane bending	$48\beta_{CCC} + 18\beta_{CNC}$
a'	563w	564w	569	CCC inplane bending	$50\beta_{CCC} + 11\beta_{NH_2}$
a'	619w		627	CCC inplane bending	$59\beta_{CCC} + 20\beta_{CH_3}$
a''	648w	649vw	658	NH <sub>2</sub> wagging/ CCC out of plane bending	$51\omega_{NH_2} + 31\eta_{CCC} + 14\tau_{NH_2}$
a''	759vs	752w	759	CH <sub>3</sub> wagging/ CCC out of plane bending	$48\omega_{CH_3} + 24\eta_{CCC} + 18\tau_{CH_3}$
a'	783m		788	CCC Ring breathing	$86\beta_{CCC}$
a''			810*	CCC out of plane bending	
a''	845s	845vw	849	C-H out of plane bending	$54\eta_{CH} + 30\eta_{CH_3}$
a''	864w	872vw	871	C-H out of plane bending	$62\eta_{CH} + 21\eta_{NH_2}$
a''	949vw	959vw	955	C-H out of plane bending	$48\eta_{CH} + 16\eta_{NH_2} + 24\eta_{CH_3}$
a'	979w	983vw	985	C-NH <sub>2</sub> stretching/ C-H out of plane bending	$70\nu_{C-NH_2} + 18\nu_{CH}$ $44\eta_{CH} + 28\eta_{CH_3} + 12\eta_{CNH_2}$
a''	1000vw		1002	C-H out of plane bending	$69\eta_{CH} + 14\eta_{CNH_2}$
a'	1032vw	1032w	1030	CCC Trigonal bending	$81\beta_{CCC}$
a'		1051vw		CH <sub>3</sub> rocking	$64\rho_{CH_3} + 29\delta_{CH_3}$
a'	1067vw	1076vw	1081	NH <sub>2</sub> rocking	$39\rho_{NH_2} + 22\rho_{CH_3} + 12\beta_{CH}$
a'	1129w	1137w	1135	C-H inplane bending	$62\beta_{CH} + 28\beta_{NH_2}$
a'	1166vw	1170vw	1170	C-H inplane bending	$66\beta_{CH} + 19\beta_{CH_3}$
a'	1194m	1199vw	1191	C-H inplane bending	$44\beta_{CH} + 18\beta_{NH_2} + 22\beta_{CH_3}$
a'	1241m	1243vw	1240	C-CH <sub>3</sub> stretching/ C-H inplane bending	$56\nu_{CCH_3} + 24\beta_{CH} + 11\beta_{C-NH_2}$
a'	1280w	1279w	1285	C-N stretching/ C-H inplane bending	$81\nu_{C-N} + 16\beta_{CH}$ $64\beta_{CH} + 21\beta_{C-NH_2}$
a'	1344m		1345	C-C stretching	$88\nu_{C-C}$
a'	1371s	1366vs	1361	C-C stretching/ CH <sub>3</sub> symmetric deformation	$74\nu_{C-C} + 11\nu_{CN}$
a'	1415w	1408vw	1415	C-C stretching	$69\nu_{C-C} + 21\nu_{C-N}$
a'	1438s		1445	C-C stretching	$79\nu_{C-C} + 12\nu_{CH}$
a'	1470vw	1464w	1468	C-C stretching/ CH <sub>3</sub> asymmetric deformation	$81\nu_{C-C} + 10\nu_{CN}$ $41\delta_{CH_3} + 28\delta_{NH_2} + 18\beta_{CH}$
a'	1518s	1517vw	1527	C=N stretching/ CH <sub>3</sub> asymmetric deformation	$79\nu_{C=N} + 12\nu_{CCH_3}$ $54\delta_{CH_3} + 38\delta_{NH_2}$
a'	1570s	1565m	1569	C=C stretching	$84\nu_{C=C}$



**Table 2.** Continue.

Species	Observed wave number		Calcd. Wave number	Assignments	% PED
	FTIR	FTR			
a'	1593vs	1593m	1598	C=C stretching	88 $\nu_{C=C}$
a'	1617s	1619vw	1628	C=C stretching/ NH <sub>2</sub> deformation	74 $\nu_{C=C}$ + 11 $\nu_{CN}$ 67 $\delta_{NH_2}$ + 28 $\delta_{CH_3}$
a'	1659s	1649vw	1652	C=C stretching	89 $\nu_{C=C}$
	1815vw			864 + 949	
	1842vw			3203 – 1371	
	1900vw			2 x 949	
	1928vw			3399 – 1470	
	1962vw			2 x 979	
	2188vw			2122 – 538	
	2382vw			2917 – 538	
	2630w			1194 – 1438	
a'	2650w		2654	C–H stretching	90 $\nu_{C-H}$
a'	2722w	2724vw	2726	C–H stretching	94 $\nu_{C-H}$
a'	2783m		2781	C–H stretching	89 $\nu_{C-H}$
a'	2873m		2876	C–H stretching	91 $\nu_{C-H}$
a'	2917m	2920m	2929	C–H stretching	90 $\nu_{C-H}$
a'		3037w	3042	C–H stretching	96 $\nu_{CH}$
a'	3060m	3062m	3066	C–H stretching	99 $\nu_{C-H}$
a'	3203s		3205	N–H symmetric stretching	94 $\nu_{N-H}$
	3334m			619 + 2722	
a'	3399s		3389	N–H asymmetric stretching	94 $\nu_{N-H}$

\*Predicted from NCA, vs: very strong, s: strong, m: medium, w: weak, vw: very weak,  $\nu$ : stretching,  $\beta$ : inplane bending,  $\delta$ : deformation:  $\eta$ : out of plane bending,  $\tau$ : twisting,  $\rho$ : rocking and  $\omega$ : wagging.

### C–NH<sub>2</sub>, C–CH<sub>3</sub> Group vibrations

The bands observed at 975 cm<sup>-1</sup> in AQ and 979 cm<sup>-1</sup> in AMQ are assigned to C–NH<sub>2</sub> stretching vibrations. The C–NH<sub>2</sub> inplane and out of plane bending vibrations in AQ are assigned at 421 and 200 cm<sup>-1</sup> respectively. Similarly, in the case of AMQ these vibrations are identified at 404 and 220 cm<sup>-1</sup> respectively. The NH<sub>2</sub> rocking mode is normally expected at 1050 cm<sup>-1</sup> and is observed in the present IR spectrum at 1067 cm<sup>-1</sup> in AMQ and at 1050 cm<sup>-1</sup> in the case of AQ. The NH<sub>2</sub> out of plane wagging mode is found in the region 550-700 cm<sup>-1</sup> and is seen in the IR spectrum at 648 and 653 cm<sup>-1</sup> in AMQ and AQ respectively. The assignments mentioned above are in good agreement with Shukla et al.<sup>27</sup> The assignment of NH<sub>2</sub> deformation vibrations in AMQ and AQ are presented in Tables 2 and 3.

Shukla et al.<sup>27</sup> assigned the C–CH<sub>3</sub> stretching modes at 1208 and 1223 cm<sup>-1</sup> in toluene and o-xylene respectively. In AMQ it is observed at 1241 cm<sup>-1</sup>. The modes observed at 325 and 280 cm<sup>-1</sup> are assigned to planar inplane bending and nonplanar out of plane bending vibrations of C–CH<sub>3</sub>, which agree favourably with Prabakaran et al.<sup>28</sup> The other characteristic modes of CH<sub>3</sub> group vibrations such as deformation, wagging, methyl asymmetric and symmetric stretching are presented in Table 2.

**Table 3.** Observed and calculated wave numbers and potential energy distribution (PED) for 5-aminoquinoline.

Species	Observed wave number		Calcd. Wave number	Assignments	% PED
	FTIR	FTR			
		83w		lattice mode	
		105vs		lattice mode	
		167vw		980 – 818	
a''		200vw	191	C-NH <sub>2</sub> out of plane bending	47 $\eta_{C-NH_2}$ + 31 $\eta_{CH}$
a''		267w	260	CNC out of plane bending	49 $\eta_{CNC}$ + 28 $\eta_{CH}$
a'		311vw	302	CCC inplane bending	34 $\beta_{CCC}$ + 31 $\beta_{CH}$
a'		318vw	311	CCC inplane bending	44 $\beta_{CCC}$ + 21 $\beta_{CCN}$
a'			337*	CNC inplane bending	
a'	421w	418vw	409	C-NH <sub>2</sub> inplane bending	48 $\beta_{C-NH_2}$ + 26 $\beta_{CH}$
a'			430*	CCN inplane bending	
a'	462m	462w	469	CCC inplane bending	51 $\beta_{CCC}$ + 38 $\beta_{CNC}$ + 11 $\beta_{CH}$
a''	478m	474w	472	CCC out of plane bending	64 $\eta_{CCC}$ + 12 $\eta_{CNC}$
a''		488vw	480	CCC out of plane bending	52 $\eta_{CCC}$ + 14 $\eta_{CCN}$ + 22 $\eta_{CH}$
a''		527vw	520	CCC out of plane bending	68 $\eta_{CCC}$ + 18 $\eta_{CNC}$
a''	570w	567vw	556	CCC out of plane bending	44 $\eta_{CCC}$ + 18 $\eta_{CCN}$ + 20 $\eta_{CH}$
a'	577w	578vw	564	CCC inplane bending	41 $\beta_{CCC}$ + 24 $\beta_{NH}$ + 16 $\beta_{CH}$
a''	653w	648vw	639	NH <sub>2</sub> wagging	49 $\omega_{NH_2}$ + 38 $\eta_{CH}$
a''	700m	708m	710	CCC out of plane bending	54 $\eta_{CCC}$ + 34 $\eta_{CNC}$
a''	729m	735vw	739	C-H out of plane bending	41 $\eta_{CH}$ + 30 $\eta_{NH_2}$
a''	750m		741	C-H out of plane bending	58 $\eta_{CH}$ + 11 $\eta_{NH_2}$
a''	793vs		784	C-H out of plane bending	54 $\eta_{CH}$ + 21 $\eta_{CCC}$
a'	827m	818vw	820	CCC ring breathing	81 $\beta_{CCC}$
a''	875w	868vw	859	C-H out of plane bending	52 $\eta_{CH}$ + 18 $\eta_{CCC}$
a''	893w	889vw	875	C-H out of plane bending	49 $\eta_{CH}$ + 29 $\eta_{C-NH_2}$
a''	950vw	949vw	939	C-H out of plane bending	54 $\eta_{CH}$ + 24 $\eta_{CCC}$
		960vw		1281 – 311	
a'	975vw	980vw	976	C-NH <sub>2</sub> stretching	64 $\nu_{C-NH_2}$ + 21 $\nu_{CH}$
a'	1013m	1008vw	1010	CCC trigonal bending	85 $\beta_{CCC}$
a'	1050m	1052w	1041	NH <sub>2</sub> rocking	51 $\rho_{NH_2}$ + 38 $\beta_{CH}$
a'	1082m	1082vw	1074	C-H inplane bending	60 $\beta_{CH}$ + 18 $\beta_{CNC}$
a'	1133vw		1125	C-H inplane bending	51 $\beta_{CH}$ + 24 $\beta_{C-NH_2}$
a'	1150vw	1149w	1141	C-H inplane bending	64 $\beta_{CH}$ + 11 $\beta_{CCC}$
a'		1172vw	1165	C-H inplane bending	48 $\beta_{CH}$ + 12 $\beta_{CCC}$
a'	1207m	1206vw	1214	C-H inplane bending	55 $\beta_{CH}$ + 24 $\beta_{CCC}$
a'		1250vw	1256	C-H inplane bending	54 $\beta_{CH}$ + 21 $\beta_{NCC}$
a'	1281m	1283vw	1280	C-N stretching	90 $\nu_{C-N}$
a'	1326m	1330vw	1338	C-C stretching	70 $\nu_{C-C}$ + 12 $\nu_{C-N}$
a'	1366s	1367s	1359	C-C stretching	78 $\nu_{C-C}$ + 11 $\nu_{C-H}$
a'	1412s	1411m	1405	C-C stretching	82 $\nu_{C-C}$ + 11 $\beta_{CCC}$
a'	1425m	1422w	1420	C-C stretching	84 $\nu_{C-C}$
a'	1465s	1467vw	1458	C-C stretching	88 $\nu_{C-C}$
a'	1507m	1509vw	1513	C=N stretching	81 $\nu_{C=N}$
		1574s	1568	1150 + 421	
a'	1586s	1587w	1581	C=C stretching	85 $\nu_{C=C}$
a'	1613m	1613vw	1613	NH <sub>2</sub> deformation	94 $\delta_{NH_2}$
a'	1658m		1651	C=C stretching	88 $\nu_{C=C}$
a'	1740vw		1734	C=C stretching	84 $\nu_{C=C}$ + 11 $\beta_{CCC}$

**Table 3.** Continue.

Species	Observed wave number		Calcd. Wave number	Assignments	% PED
	FTIR	FTR			
a'	1770vw		1761	C=C stretching	90 $\nu_{C=C}$
	1827vw			3033 - 1207	
	1898vw			2 x 950	
	1917vw			3332 - 1412	
	1950vw			1050 + 893	
	2272vw			2 x 1133	
	2420vw			2 x 1207	
	2783vw			1574 + 1207	
a'	2916vw		2909	C-H stretching	86 $\nu_{C-H}$
a'	2971vw	2972vw	2971	C-H stretching	91 $\nu_{C-H}$
a'		3008vw	3012	C-H stretching	94 $\nu_{C-H}$
a'	3033w	3033vw	3029	C-H stretching	97 $\nu_{C-H}$
a'		3067w	3061	C-H stretching	82 $\nu_{C-H}$
a'	3080w	3080w	3071	C-H stretching	88 $\nu_{C-H}$
		3190vw		2 x 1587	
a'	3203s		3210	N-H symmetric stretching	91 $\nu_{NH2}$
a'	3332m		3331	N-H asymmetric stretching	94 $\nu_{NH2}$

\*Predicted from normal coordinate analysis, vs: very strong, s: strong, m: medium, w: weak, vw: very weak,  $\nu$ : stretching,  $\beta$ : inplane bending,  $\delta$ : deformation,  $\eta$ : out of plane bending,  $\tau$ : twisting,  $\omega$ : wagging and  $\rho$ : rocking.

## N-H Stretching

The molecules under consideration have only 1 NH<sub>2</sub> group and hence we expect 1 N-H asymmetric and N-H symmetric stretching vibrations. In the primary aromatic amines, the N-H stretching frequency occurs in the region 3300–3500 cm<sup>-1</sup>. Hence the absorption bands observed at 3399 and 3203 cm<sup>-1</sup> in AMQ and at 3332 and 3203 cm<sup>-1</sup> in AQ are assigned to N-H asymmetric and symmetric stretching modes in the NH<sub>2</sub> group respectively. These observations agree very well with a large number of studies.<sup>29,30</sup>

The rest of the observed frequencies may be accounted for as resulting from the allowed combinations of selected fundamentals, as indicated in Tables 2 and 3.

## Potential energy distribution

To check whether the chosen set of assignments contribute the most to the potential energy associated with the normal coordinates of the molecules, the potential energy distribution (PED) has been calculated using the relation

$$PED = \frac{F_{ii}L_{ik}^2}{\lambda_k}$$

where PED is the contribution of the  $i^{th}$  symmetry coordinate to the potential energy of the vibrations, whose frequency is  $\nu_k$ ,  $F_{ii}$  is the force constant evaluated by the damped least square technique,  $L_{ik}$  is the normalised amplitude of the associated element (i,k) and  $\lambda_k$  is the eigen value corresponding to the

vibrational frequency  $k$  ( $\lambda_k = 4\pi^2c^2\nu_k^2$ ). The PED contribution values corresponding to each of the observed frequencies are listed in Tables 2 and 3.

## Conclusion

Complete vibrational spectral assignments and analyses are available in the present work for 4-aminoquinaldine and 5-aminoquinoline molecules. The close agreement between the observed and calculated frequencies confirms the validity and precision of the present assignments. The purity of the modes is ascertained by the potential energy distribution associated with each frequency of vibration.

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