



## **SPECTROSCOPIC INVESTIGATIONS AND COMPUTATIONAL STUDY OF ANILINE ACETATE**

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### **ABSTRACT**

Fourier transform infrared (FT-IR) and Fourier transform (FT) Raman spectra of aniline acetate were recorded and analyzed. The vibrational frequencies of aniline acetate were calculated using Gaussian03 software package and the fundamental modes are assigned. The calculated frequencies are in agreement with the experimental values. The calculated geometrical parameters are compared with the geometrical parameters of similar derivatives. The first hyperpolarizability, infrared intensities and Raman activities are reported. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non linear optics

**Keywords:** Aniline, Acetate, HF calculations, Hyperpolarizability

### **INTRODUCTION**

Aniline and its derivatives are used in several pharmaceutical and industrial processes as starting materials because they can serve as precursors in the synthesis of dyes and sensitizer molecules, pesticides and antioxidants<sup>1,2</sup>. They are used in electro optical industry, for the synthesis of technological materials with nonlinear optical responses<sup>3</sup>. The structures and vibrational spectra of aniline and substituted aniline complexes are being studied extensively, since elucidation of their molecular properties as well as nature of

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reaction mechanism is of utmost importance. The structural, electronic and vibrational parameters of aniline molecule change with inclusion of substituent group because it leads to the variation of charge distribution in the molecule. The structure and normal vibration of aniline and its derivatives were reported by Tzeng et al.<sup>4,5</sup> Vibrational spectroscopic study of acetate group is reported by Ibrahim and Koglin<sup>6</sup>. In the present study, the FT-IR, FT-Raman and theoretical calculations of the wavenumber values of the title compound are reported.

## EXPERIMENTAL

The FT-IR spectrum was recorded using a Bruker IFS 28 spectrometer with KBr pellets, number of scans 16, resolution  $2\text{ cm}^{-1}$ . The FT-Raman spectrum was obtained on a Bruker Equinox 55/s spectrometer with FRA Raman socket, 106/s. For excitation of the spectrum, the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, laser power 250 mW, resolution  $2\text{ cm}^{-1}$ , number of scans 128.

### Computational details

Calculations of the title compound were carried out with Gaussian03 program<sup>7</sup> using the HF/6-31G\* basis set to predict the molecular structure and wavenumbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minimum on the potential surface. The wavenumber values computed at the Hartree-Fock level contain known systematic errors due to the negligence of electron correlation<sup>8</sup>. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G\* basis set<sup>8</sup>. The absence of imaginary wavenumber on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The spectral assignment was aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes.

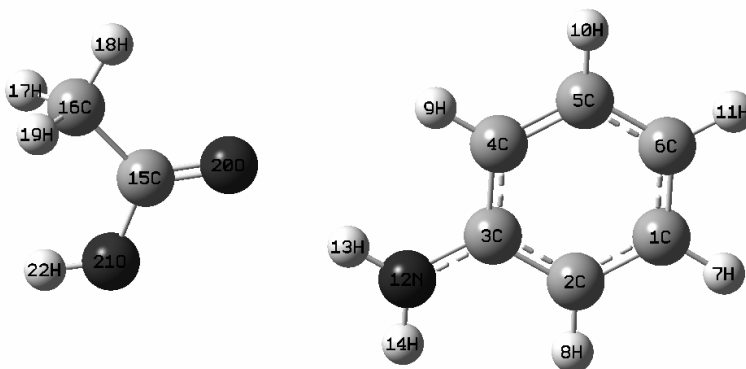
## RESULTS AND DISCUSSION

The calculated (scaled) wavenumbers, infrared and Raman bands and the corresponding assignments are given in Table 1.

### Acetate group vibrations

Methyl groups are generally referred to as electron donating substituents in the aromatic ring system.<sup>9</sup> In acetates, the asymmetric vibrations of the methyl group are expected in the region  $2930 - 3040\text{ cm}^{-1}$  and symmetric vibrations in the region  $2960-2860$

$\text{cm}^{-1}$ , and usually the bands are weak.<sup>10</sup> Aromatic acetyl substituents absorb in a narrow range  $3000 - 3020 \text{ cm}^{-1}$  and absorption sometimes coincides with a CH stretching mode of the ring.<sup>10</sup> In the present case, the asymmetric methyl bands are calculated to be at  $2974, 2918 \text{ cm}^{-1}$  (HF) and experimentally, a band is observed in the Raman spectrum at  $2932 \text{ cm}^{-1}$  and at  $2975, 2914 \text{ cm}^{-1}$  in the IR spectrum. The symmetric methyl stretching vibration is observed at  $2857 \text{ cm}^{-1}$  in the IR spectrum and at  $2860 \text{ cm}^{-1}$  theoretically. As contrasted with the weak absorptions of methyl stretching vibrations, the methyl symmetric deformation absorb moderately to strongly in the range  $1350-1390 \text{ cm}^{-1}$  and asymmetric methyl deformations in the region<sup>10</sup>  $1410-14653 \text{ cm}^{-1}$ . The HF calculations give  $1459, 1466$  and  $1406 \text{ cm}^{-1}$  as asymmetric and symmetric methyl deformation bands, respectively. The bands observed at  $1448, 1435$  and  $1393 \text{ cm}^{-1}$  in IR is assigned as deformation bands of the methyl group. According to Colthup<sup>11</sup>, in acetates the methyl next to the C=O absorbs near  $1374 \text{ cm}^{-1}$  due to the symmetric deformation; the asymmetric methyl deformation absorbs weakly near  $1430 \text{ cm}^{-1}$ . The methyl rocking generally appear in the regions  $1020-1080$  and  $935-1025 \text{ cm}^{-1}$ , as a weak, moderate or sometimes strong band, the wavenumber of which is coupled to the CC stretching vibrations, which occurs in the neighborhood of  $900 \text{ cm}^{-1}$ . With acetates, the rocking modes are clearly separated and show weak to medium activity in the region<sup>10</sup>  $1050 \pm 30$  and  $980 \pm 45 \text{ cm}^{-1}$ . The bands at  $1075 \text{ cm}^{-1}$  in Raman and at  $1069, 989 \text{ cm}^{-1}$  (HF) are assigned as rocking modes of the methyl group. New pane in O bonded – C(=O)Me group,<sup>10</sup> the C=O stretching vibration exhibits a strong band at  $1750 \pm 20 \text{ cm}^{-1}$ . Esters and lactones have two characteristically strong absorption bands arising from C=O and C-O stretching. The intense C=O stretching vibration occurs at higher frequencies than that of normal lactones. The force constant of the carbonyl bond is increased by the electron-attracting nature of the adjacent oxygen atom due to inductive effect.<sup>11</sup> In the present case, the stretching mode  $\nu\text{C=O}$  is observed at  $1679 \text{ cm}^{-1}$  in Raman spectrum and the calculated value for this mode is  $1721 \text{ cm}^{-1}$ . The C-O next to the carbonyl is stiffer than the other single bonds due to resonance, which tends to localize the high vibration in the C-O bond. Acetates show a strong vibration in the region  $1260-1320 \text{ cm}^{-1}$  as  $\nu\text{C-O}$  band.<sup>11</sup> For phenyl acetate<sup>12</sup>, the  $\nu\text{CC(=O)O}$  stretching band is observed at  $1215 \text{ cm}^{-1}$ . The band at  $1235 \text{ cm}^{-1}$  in the Raman spectrum and  $1237 \text{ cm}^{-1}$  (HF) is assigned as  $\nu\text{C(=O)O}$  for the title compound. The bands calculated at  $584$  and  $413 \text{ cm}^{-1}$  are assigned as the deformation bands of C=O. For acetate group<sup>6,13</sup>, the deformation bands of C=O are reported at  $642$  and  $581 \text{ cm}^{-1}$  experimentally. In the present case, the C-C stretching mode of the acetate group is at  $1022 \text{ cm}^{-1}$  theoretically. The  $\nu\text{CC}$  mode is reported at  $847 \text{ cm}^{-1}$  experimentally, and at  $866 \text{ cm}^{-1}$  theoretically.<sup>6</sup> The HF calculations give band at  $416 \text{ cm}^{-1}$  as skeletal deformations of O-bonded –C(=O)Me group and the torsional vibrations are observed below  $500 \text{ cm}^{-1}$ .



### Aniline group vibrations

The  $\text{NH}_2$  stretching modes are expected in the region<sup>10</sup>  $3250\text{--}3480\text{ cm}^{-1}$ . The HF calculations give  $3552$  and  $3418\text{ cm}^{-1}$  as asymmetric and symmetric  $\text{NH}_2$  stretching vibrations. The  $\text{NH}_2$  scissoring vibration<sup>10</sup> is expected in the range  $1620 \pm 20\text{ cm}^{-1}$  and the band at  $1663\text{ cm}^{-1}$  in IR spectrum,  $1665\text{ cm}^{-1}$  in Raman and  $1657\text{ cm}^{-1}$  (HF) is assigned as this scissoring mode. The  $\text{NH}_2$  scissoring modes are reported at  $1629\text{ cm}^{-1}$  for sulfanilamide<sup>14</sup> and at  $1637\text{ cm}^{-1}$  in IR,  $1634\text{ cm}^{-1}$  in Raman and  $1642\text{ cm}^{-1}$  theoretically for orthanilic acid.<sup>15</sup> The  $\delta\text{NH}_2$  scissoring modes are reported at  $1621$ ,  $1597\text{ cm}^{-1}$  (IR),  $1621$ ,  $1602\text{ cm}^{-1}$  (Raman) for para substituted halogenoanilines<sup>16</sup> and at  $1630\text{ cm}^{-1}$  for 2-aminobenzyl alcohol.<sup>17</sup> According to Roeges<sup>10</sup>,  $\rho/\tau\text{NH}_2$  vibration is expected in the region  $1070 \pm 50\text{ cm}^{-1}$  and in the present case, the band observed at  $1105\text{ cm}^{-1}$  in IR and  $1100\text{ cm}^{-1}$  by HF calculation is assigned as  $\rho/\tau\text{NH}_2$  mode. Krishnakumar and Balachandran<sup>18</sup> and Altun *et al.*<sup>19</sup> reported these modes at  $1130$ ,  $1126$ ,  $1089$ ,  $1085\text{ cm}^{-1}$  for dibromo, nitro and methyl thioaniline complexes, and at  $1040$ ,  $1030$ ,  $1008\text{ cm}^{-1}$  for methyl aniline complexes, respectively. Kurt *et al.*<sup>20</sup> observed the wagging mode  $\omega\text{NH}_2$  for chloromethylaniline at  $667\text{ cm}^{-1}$  in IR spectrum and at  $695\text{ cm}^{-1}$  by HF calculation. Tzeng *et al.*<sup>4</sup> calculated the wagging mode of amino group at  $649\text{ cm}^{-1}$  and experimentally at  $665\text{ cm}^{-1}$ . For the title compound, the wagging mode of  $\text{NH}_2$  is observed at  $607\text{ cm}^{-1}$  in the IR spectrum,  $619\text{ cm}^{-1}$  in Raman and at  $616\text{ cm}^{-1}$  theoretically.

Primary aromatic amines with nitrogen directly attached to the ring absorb in the region  $1330\text{--}1260\text{ cm}^{-1}$  due to the stretching vibration of the phenyl carbon-nitrogen bond.<sup>4,11</sup> We have observed this  $\nu\text{CN}$  mode at  $1240\text{ cm}^{-1}$  theoretically. Akalin and Akyuz<sup>21</sup> assigned C-N stretching vibration at  $1268\text{ cm}^{-1}$  in the Raman spectrum for paraphenylenediamine, at

1226, 1227, 1229  $\text{cm}^{-1}$  for paraphenyldiamine complexes and at 1266, 1263, 1216  $\text{cm}^{-1}$  theoretically. The torsional modes<sup>10</sup> of  $\text{NH}_2$  are expected in the region  $230 \pm 70 \text{ cm}^{-1}$ .

### Phenyl ring vibrations

The existence of one or more aromatic rings in a structure is normally readily determined from the C H and C=C-C ring related vibrations. The CH stretching occurs above 3000  $\text{cm}^{-1}$  and is typically exhibited as a multiplicity of weak to moderate bands compared with aliphatic C-H stretch.<sup>22</sup> In the present case, the HF calculations predict the  $\nu_{\text{CH}}$  modes in the range 2982-3021  $\text{cm}^{-1}$ . Experimentally observed values are in the range 3022-3135  $\text{cm}^{-1}$ . The lowering of CH stretching mode is due to the interaction between acetate group and the phenyl ring. The benzene ring possesses six ring stretching vibrations of which the four with the highest wavenumbers occurring near 1600, 1580, 1490 and 1440  $\text{cm}^{-1}$  are good group vibrations.<sup>10</sup> With heavy substituents, the bands tend to shift to somewhat lower wavenumbers and the greater the number of substituents on the ring, the broader are the absorption regions.<sup>10</sup> In the case of C=O substitution, the band near 1490  $\text{cm}^{-1}$  can be very weak.<sup>10</sup> The fifth ring stretching vibration is active near  $1315 \pm 65 \text{ cm}^{-1}$ , a region that overlaps strongly with that of the CH in-plane deformation.<sup>10</sup> The sixth ring stretching vibration, the ring breathing mode appears as a weak band near 1000  $\text{cm}^{-1}$  in mono-, 1,3-di and 1,3,5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from other modes. For the title compound, the ring breathing mode appears at 999  $\text{cm}^{-1}$  in the IR spectrum, 1004  $\text{cm}^{-1}$  in the Raman spectrum and at 1012  $\text{cm}^{-1}$  theoretically. The in-plane and out-of-plane CH deformations of the phenyl ring are expected in the regions 1320-1040  $\text{cm}^{-1}$  and 990-730  $\text{cm}^{-1}$ , respectively.<sup>10</sup> All these bands are identified and assigned (Table 1).

**Table 1: Calculated vibrational wavenumbers (scaled), measured infrared band positions and assignments for aniline acetate**

$\nu_{(\text{HF})}$ $\text{cm}^{-1}$	IR Intensity (KM/Mole)	Raman activity ( $\text{A}^{**4}/\text{AMU}$ )	$\nu_{(\text{IR})}$ $\text{cm}^{-1}$	$\nu_{(\text{Raman})}$ $\text{cm}^{-1}$	Assignments
3598	106.36	85.86			$\nu_{\text{OH}}$
3552	100.55	59.07			$\nu_{\text{asNH}_2}$
3418	259.44	226.45	3293	3300	$\nu_{\text{sNH}_2}$
3021	19.29	276.65	3135	3100	$\nu_{\text{CH}}$
3007	38.60	23.64	3081		$\nu_{\text{CH}}$

Cont...

$\nu_{(\text{HF})}$ $\text{cm}^{-1}$	IR Intensity (KM/Mole)	Raman activity ( $\text{A}^{**4}/\text{AMU}$ )	$\nu_{(\text{IR})}$ $\text{cm}^{-1}$	$\nu_{(\text{Raman})}$ $\text{cm}^{-1}$	Assignments
2998	36.92	99.86	3059	3050	$\nu\text{CH}$
2986	0.83	111.05	3022		$\nu\text{CH}$
2982	2.07	48.70			$\nu\text{CH}$
2979	15.94	36.16	2975		$\nu_{\text{as}}\text{CH}_3$
2918	6.94	70.46	2914	2932	$\nu_{\text{as}}\text{CH}_3$
2860	5.51	154.50	2857		$\nu_{\text{s}}\text{CH}_3$
1721	505.24	29.32		1679	$\nu\text{C}=\text{O}$
1657	101.16	7.27	1663	1665	$\delta\text{NH}_2$
1600	190.95	65.57	1620	1605	$\nu\text{Ph}$
1580	14.59	7.38	1599	1543	$\nu\text{Ph}$
1492	117.36	0.94	1501	1505	$\nu\text{Ph}$
1465	0.64	1.12	1489		$\nu\text{Ph}$
1459	16.41	11.31	1448		$\delta_{\text{as}}\text{CH}_3$
1446	13.94	15.73	1435	1450	$\delta_{\text{as}}\text{CH}_3$
1406	30.88	2.81	1393		$\delta_{\text{s}}\text{CH}_3$
1358	1.28	0.46	1369	1371	$\nu\text{Ph}$
1273	113.97	21.18	1266	1288	$\delta\text{CH}$
1240	18.62	1.12			$\nu\text{CN}$
1237	339.28	0.08		1235	$\nu\text{C}(=\text{O})\text{O}$
1178	17.13	2.35	1180	1179	$\delta\text{CH}$
1147	16.30	5.65		1153	$\delta\text{CH}$
1143	126.75	5.09		1130	$\delta\text{OH}$
1100	13.90	0.90		1105	$\rho/\tau\delta\text{NH}_2$
1069	12.611	1.05		1075	$\rho\text{CH}_3$
1045	2.57	0.73	1042	1057	$\delta\text{CH}$

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$\nu_{(\text{HF})}$ $\text{cm}^{-1}$	IR Intensity (KM/Mole)	Raman activity ( $\text{A}^{**4}/\text{AMU}$ )	$\nu_{(\text{IR})}$ $\text{cm}^{-1}$	$\nu_{(\text{Raman})}$ $\text{cm}^{-1}$	Assignments
1022	0.17	0.36			$\nu_{\text{CC}}$
1019	0.03	0.04	1014		$\delta_{\text{CH}}$
1012	1.04	6.84	999	1004	Ring breath
989	3.38	5.06			$\rho_{\text{CH}_3}$
982	20.67	61.65		984	$\gamma_{\text{CH}}$
924	29.58	0.01	952	943	$\gamma_{\text{CH}}$
857	0.08	0.60		857	$\gamma_{\text{CH}}$
830	38.76	13.39			$\gamma_{\text{CH}}$
804	8.08	25.73	760		$\delta_{\text{Ph(X)}}$
780	139.47	2.38	755	768	$\gamma_{\text{CH}}$
704	48.77	0.10	694		$\gamma_{\text{Ph}}$
627	1.01	5.69		633	$\delta_{\text{Ph(X)}}$
616	211.55	1.02	607	619	$\omega_{\text{NH}_2}$
584	7.21	1.03			$\delta_{\text{C=O}}$
574	20.47	3.79		565	$\delta_{\text{OC(O)}}$
527	0.30	6.37	534	532	$\delta_{\text{Ph(X)}}$
519	17.42	0.18	511		$\gamma_{\text{Ph(X)}}$
434	218.36	1.43		435	$\gamma_{\text{OH}}$
422	1.11	0.01			$\gamma_{\text{Ph}}$
413	7.15	1.26			$\gamma_{\text{C=O}}$
382	4.44	1.02		387	$\delta_{\text{C-C-O}}$
351	114.73	0.59		349	$t_{\text{NH}_2}$
224	3.05	0.53		190	$\delta_{\text{C-O}}$
108	0.33	0.30			$t_{\text{C(=O)CH}_3}$
82	3.13	0.86			$t_{\text{CH}_3}$

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$\nu_{(\text{HF})}$ $\text{cm}^{-1}$	IR Intensity (KM/Mole)	Raman activity ( $\text{A}^{**4}/\text{AMU}$ )	$\nu_{(\text{IR})}$ $\text{cm}^{-1}$	$\nu_{(\text{Raman})}$ $\text{cm}^{-1}$	Assignments
53	1.93	6.63			$\gamma\text{Ph(X)}$
27	1.93	0.14			$\delta\text{Ph(X)}$
22	1.31	0.67			tPh
17	12.37	0.17			tPh
8	7.07	0.12			tPh

$\nu$ -stretching;  $\delta$ -in-plane deformation;  $\gamma$ -out-of-plane deformation;  $\tau$ -twisting;  $\rho$ -rocking;  $\omega$  -wagging; t- torsion; X-substituent sensitive; Ph-Phenyl; subscripts: as – asymmetric, s- symmetric

### Geometrical parameters and hyperpolarizability

According to Anderson *et al.*<sup>23</sup> the CN bond lengths are in the range 1.472-1.467 Å. The CCN bond angles are reported<sup>23</sup> as 118.6- 119.5°. For the title compound, the CCN angles  $\text{C}_4\text{-C}_3\text{-N}_{12} = 120.5^\circ$  and  $\text{C}_2\text{-C}_3\text{-N}_{12} = 121.1^\circ$ . In the amino group, the nitrogen atom is likely out-of-plane, with a torsional angle C-C-C-N around 180°. Existence of this angle has been interpreted to be caused by the asymmetric interaction between the  $\text{NH}_2$  group and the benzene ring plane. This interaction is common to all aniline derivatives.<sup>4,24</sup> The C-N distance in the present case is 1.3769 Å, which is similar to the measured value in aniline.<sup>25</sup> For acetate group, Ibrahim and Koglin<sup>6</sup> reported the  $\text{C}_{15}\text{-C}_{16}$ ,  $\text{C}_{16}\text{-H}_{17-19}$ ,  $\text{C}_{15}\text{-O}_{21}$  and  $\text{C}_{15}=\text{O}_{20}$  bond lengths as 1.52, 1.102, 1.364 and 1.214 Å, respectively, whereas in the present case, the corresponding values are 1.4989, 1.0773-1.0842, 1.3560 and 1.2057 Å. For the title compound, the bond angles of the acetate group,  $\text{C}_{16}\text{-C}_{15}\text{-O}_{20} = 124.5^\circ$ ,  $\text{O}_{21}\text{-C}_{15}\text{-O}_{20} = 119.0.0^\circ$ ,  $\text{C}_{15}\text{-C}_{16}\text{-H}_{17-19} = 109.3\text{-}110.5^\circ$ , which are in agreement with the values 113, 126.6, 122 and 107° for acetate<sup>6</sup>.

Analysis of organic molecules having conjugated  $\pi$ -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research.<sup>26</sup> The potential application of the title compound in the field of non linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement. The first hyperpolarizability ( $\beta_0$ ) of this novel molecular system is calculated using HF method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a  $3 \times 3 \times 3$  matrix. The 27



components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry.<sup>27</sup> The calculated first hyperpolarizability of the title compound is  $4.41 \times 10^{-30}$  esu, which is comparable with the reported values of similar derivatives<sup>28</sup> and experimental evaluation of this data is not readily available. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

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