



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^{1,2}. They are used in electro optical industry, for the synthesis of technological materials with nonlinear optical responses³. 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.^{4,5} Vibrational spectroscopic study of acetate group is reported by Ibrahim and Koglin⁶. 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 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 cm^{-1} , number of scans 128.

Computational details

Calculations of the title compound were carried out with Gaussian03 program⁷ 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 correlation⁸. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G* basis set⁸. 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.

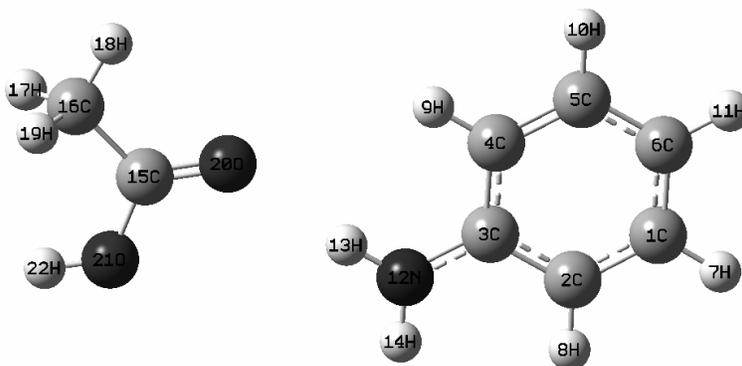
RESULTS AND DISCUSSION

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.⁹ 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 $2960-2860$

cm^{-1} , and usually the bands are weak.¹⁰ 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.¹⁰ In the present case, the asymmetric methyl bands are calculated to be at 2974, 2918 cm^{-1} (HF) and experimentally, a band is observed in the Raman spectrum at 2932 cm^{-1} and at 2975, 2914 cm^{-1} in the IR spectrum. The symmetric methyl stretching vibration is observed at 2857 cm^{-1} in the IR spectrum and at 2860 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 region¹⁰ $1410-14653 \text{ cm}^{-1}$. The HF calculations give 1459, 1466 and 1406 cm^{-1} as asymmetric and symmetric methyl deformation bands, respectively. The bands observed at 1448, 1435 and 1393 cm^{-1} in IR is assigned as deformation bands of the methyl group. According to Colthup¹¹, in acetates the methyl next to the C=O absorbs near 1374 cm^{-1} due to the symmetric deformation; the asymmetric methyl deformation absorbs weakly near 1430 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 cm^{-1} . With acetates, the rocking modes are clearly separated and show weak to medium activity in the region¹⁰ 1050 ± 30 and $980 \pm 45 \text{ cm}^{-1}$. The bands at 1075 cm^{-1} in Raman and at 1069, 989 cm^{-1} (HF) are assigned as rocking modes of the methyl group. New pane in O bonded – C(=O)Me group,¹⁰ 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.¹¹ In the present case, the stretching mode $\nu\text{C=O}$ is observed at 1679 cm^{-1} in Raman spectrum and the calculated value for this mode is 1721 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.¹¹ For phenyl acetate¹², the $\nu\text{CC(=O)O}$ stretching band is observed at 1215 cm^{-1} . The band at 1235 cm^{-1} in the Raman spectrum and 1237 cm^{-1} (HF) is assigned as $\nu\text{C(=O)O}$ for the title compound. The bands calculated at 584 and 413 cm^{-1} are assigned as the deformation bands of C=O. For acetate group^{6,13}, the deformation bands of C=O are reported at 642 and 581 cm^{-1} experimentally. In the present case, the C-C stretching mode of the acetate group is at 1022 cm^{-1} theoretically. The νCC mode is reported at 847 cm^{-1} experimentally, and at 866 cm^{-1} theoretically.⁶ The HF calculations give band at 416 cm^{-1} as skeletal deformations of O-bonded –C(=O)Me group and the torsional vibrations are observed below 500 cm^{-1} .



Aniline group vibrations

The NH_2 stretching modes are expected in the region¹⁰ $3250\text{--}3480\text{ cm}^{-1}$. The HF calculations give 3552 and 3418 cm^{-1} as asymmetric and symmetric NH_2 stretching vibrations. The NH_2 scissoring vibration¹⁰ is expected in the range $1620 \pm 20\text{ cm}^{-1}$ and the band at 1663 cm^{-1} in IR spectrum, 1665 cm^{-1} in Raman and 1657 cm^{-1} (HF) is assigned as this scissoring mode. The NH_2 scissoring modes are reported at 1629 cm^{-1} for sulfanilamide¹⁴ and at 1637 cm^{-1} in IR, 1634 cm^{-1} in Raman and 1642 cm^{-1} theoretically for orthanilic acid.¹⁵ The δNH_2 scissoring modes are reported at 1621 , 1597 cm^{-1} (IR), 1621 , 1602 cm^{-1} (Raman) for para substituted halogenoanilines¹⁶ and at 1630 cm^{-1} for 2-aminobenzyl alcohol.¹⁷ According to Roeges¹⁰, $\rho/\tau\text{NH}_2$ vibration is expected in the region $1070 \pm 50\text{ cm}^{-1}$ and in the present case, the band observed at 1105 cm^{-1} in IR and 1100 cm^{-1} by HF calculation is assigned as $\rho/\tau\text{ NH}_2$ mode. Krishnakumar and Balachandran¹⁸ and Altun *et al.*¹⁹ reported these modes at 1130 , 1126 , 1089 , 1085 cm^{-1} for dibromo, nitro and methyl thioaniline complexes, and at 1040 , 1030 , 1008 cm^{-1} for methyl aniline complexes, respectively. Kurt *et al.*²⁰ observed the wagging mode $\omega\text{ NH}_2$ for chloromethylaniline at 667 cm^{-1} in IR spectrum and at 695 cm^{-1} by HF calculation. Tzeng *et al.*⁴ calculated the wagging mode of amino group at 649 cm^{-1} and experimentally at 665 cm^{-1} . For the title compound, the wagging mode of NH_2 is observed at 607 cm^{-1} in the IR spectrum, 619 cm^{-1} in Raman and at 616 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.^{4,11} We have observed this νCN mode at 1240 cm^{-1} theoretically. Akalin and Akyuz²¹ assigned C-N stretching vibration at 1268 cm^{-1} in the Raman spectrum for paraphenylenediamine, at

1226, 1227, 1229 cm^{-1} for paraphenyldiamine complexes and at 1266, 1263, 1216 cm^{-1} theoretically. The torsional modes¹⁰ of 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 cm^{-1} and is typically exhibited as a multiplicity of weak to moderate bands compared with aliphatic C-H stretch.²² In the present case, the HF calculations predict the ν_{CH} modes in the range 2982-3021 cm^{-1} . Experimentally observed values are in the range 3022-3135 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 cm^{-1} are good group vibrations.¹⁰ 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.¹⁰ In the case of C=O substitution, the band near 1490 cm^{-1} can be very weak.¹⁰ 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.¹⁰ The sixth ring stretching vibration, the ring breathing mode appears as a weak band near 1000 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 cm^{-1} in the IR spectrum, 1004 cm^{-1} in the Raman spectrum and at 1012 cm^{-1} theoretically. The in-plane and out-of-plane CH deformations of the phenyl ring are expected in the regions 1320-1040 cm^{-1} and 990-730 cm^{-1} , respectively.¹⁰ All these bands are identified and assigned (Table 1).

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

$\nu_{(\text{HF})}$ cm^{-1}	IR Intensity (KM/Mole)	Raman activity ($\text{A}^{**4}/\text{AMU}$)	$\nu_{(\text{IR})}$ cm^{-1}	$\nu_{(\text{Raman})}$ cm^{-1}	Assignments
3598	106.36	85.86			ν_{OH}
3552	100.55	59.07			ν_{asNH_2}
3418	259.44	226.45	3293	3300	ν_{sNH_2}
3021	19.29	276.65	3135	3100	ν_{CH}
3007	38.60	23.64	3081		ν_{CH}

Cont...

$\nu_{(\text{HF})}$ cm^{-1}	IR Intensity (KM/Mole)	Raman activity ($\text{A}^{**4}/\text{AMU}$)	$\nu_{(\text{IR})}$ cm^{-1}	$\nu_{(\text{Raman})}$ cm^{-1}	Assignments
2998	36.92	99.86	3059	3050	νCH
2986	0.83	111.05	3022		νCH
2982	2.07	48.70			νCH
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	δNH_2
1600	190.95	65.57	1620	1605	νPh
1580	14.59	7.38	1599	1543	νPh
1492	117.36	0.94	1501	1505	νPh
1465	0.64	1.12	1489		νPh
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	νPh
1273	113.97	21.18	1266	1288	δCH
1240	18.62	1.12			νCN
1237	339.28	0.08		1235	$\nu\text{C}(=\text{O})\text{O}$
1178	17.13	2.35	1180	1179	δCH
1147	16.30	5.65		1153	δCH
1143	126.75	5.09		1130	δOH
1100	13.90	0.90		1105	$\rho/\tau\delta\text{NH}_2$
1069	12.611	1.05		1075	ρCH_3
1045	2.57	0.73	1042	1057	δCH

Cont...

$\nu_{(\text{HF})}$ cm^{-1}	IR Intensity (KM/Mole)	Raman activity ($\text{A}^{**4}/\text{AMU}$)	$\nu_{(\text{IR})}$ cm^{-1}	$\nu_{(\text{Raman})}$ cm^{-1}	Assignments
1022	0.17	0.36			ν_{CC}
1019	0.03	0.04	1014		δ_{CH}
1012	1.04	6.84	999	1004	Ring breath
989	3.38	5.06			ρ_{CH_3}
982	20.67	61.65		984	γ_{CH}
924	29.58	0.01	952	943	γ_{CH}
857	0.08	0.60		857	γ_{CH}
830	38.76	13.39			γ_{CH}
804	8.08	25.73	760		$\delta_{\text{Ph(X)}}$
780	139.47	2.38	755	768	γ_{CH}
704	48.77	0.10	694		γ_{Ph}
627	1.01	5.69		633	$\delta_{\text{Ph(X)}}$
616	211.55	1.02	607	619	ω_{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	γ_{OH}
422	1.11	0.01			γ_{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_{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_{CH_3}

Cont...

$\nu_{(\text{HF})}$ cm^{-1}	IR Intensity (KM/Mole)	Raman activity ($\text{A}^{**4}/\text{AMU}$)	$\nu_{(\text{IR})}$ cm^{-1}	$\nu_{(\text{Raman})}$ 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

ν -stretching; δ -in-plane deformation; γ -out-of-plane deformation; τ -twisting; ρ -rocking; ω -wagging; t- torsion; X-substituent sensitive; Ph-Phenyl; subscripts: as – asymmetric, s- symmetric

Geometrical parameters and hyperpolarizability

According to Anderson *et al.*²³ the CN bond lengths are in the range 1.472-1.467 Å. The CCN bond angles are reported²³ 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 NH_2 group and the benzene ring plane. This interaction is common to all aniline derivatives.^{4,24} The C-N distance in the present case is 1.3769 Å, which is similar to the measured value in aniline.²⁵ For acetate group, Ibrahim and Koglin⁶ 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 acetate⁶.

Analysis of organic molecules having conjugated π -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research.²⁶ 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 (β_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.²⁷ The calculated first hyperpolarizability of the title compound is 4.41×10^{-30} esu, which is comparable with the reported values of similar derivatives²⁸ 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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