Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(10):4628-4636

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Spectroscopic and Thermal studies of Anthralinic acid (Vitamin *l*)-with Br and Cl

V. Susindran[a,c], S. Athimoolam[b] and S. Asath Bahadur[a#]

[a]Department of Physics, Kalasalingam University, Anand Nagar, Krishnan Koil - 626 190, Tamil Nadu, India.
[b]Department of Physics, University College of Engineering Nagercoil, Anna University, Tirunelveli, Nagercoil - 629 004, Tamil Nadu, India,
[c]Directorate of Lighthouses & Lightships, Ministry of Shipping, Nagapattinam Lighthouse & DGPS station, Nagapattinam – 611 001, Tamil Nadu India

---

ABSTRACT

The infrared (IR) and Raman spectra were recorded at room temperature of 2-Carboxyanilinium Bromide and 2-Carboxyanilinium Chloride and observed band were assigned. In the present study, anthranilic acid is observed as a protonated carboxyanilinium cation with a bromide, chloride as anion and hydrogen-bonded water molecule. The proposed assignments of normal modes are based on group theoretical analysis. The extensive intermolecular hydrogen bonding in the crystal has been identified by the shifting of bands due to the stretching and bending modes of the various functional groups. Thermal stability and phase transition study has been analyzed by TG/DTA.

Key words: 2-aminobenzoic acid, infrared spectra, Raman spectra, TG/DTA, intermolecular hydrogen bonding

---

INTRODUCTION

Anthranilic acid (2-aminobenzoic acid) is an important and versatile starting material for the synthesis of benzofused heterocycles and other molecules. It also plays an important role in the biosynthesis of tryptophan, tyrosine, phenylalanine, and several types of alkaloids. Anthranilic acid exhibits an amethyst fluorescence when dissolved in ether, alcohol or glycerol [1]. It has properties that can be used for bioanalytical purposes such as monitoring the glycosylation of proteins [2]. Anthranilic acid is an amphoteric compound like other amino acids, which behaves as an acid and base [3]. An intramolecular proton exchange has been documented, which occurs in anthralinic acid between the amine and carboxylic acid [4]. It contains a hydrogen acceptor and a hydrogen donor that are in a conjugated system.

It is used as an intermediate for the production of dyes, pigments and saccharin, and its esters are used in preparing perfumes, pharmaceuticals and UV-absorber as well as corrosion inhibitors for metals and mould inhibitors in Soya sauce. It is also known to be a specific precursor of the skimmianine and acronidine alkaloids [5]. Anthranilic acid and its derivatives are used as the preferred fluorescent labels for carbohydrate analysis with very high sensitivity and for specific labeling of the reducing mono and oligosaccharides [6,7]. Anthranilic acid occurs either as a positively [8] or a negatively charged ion or as a neutral molecule (also as a zwitterions) depending on the environment and pH of the solution[9,10]. There have been many reports on the metal-anthranilate complexes along with the structure of many oh these compounds. Some transition metal anthranilates have capability for hydrogenation [11,12]. In the present investigation, the vibrational spectra of 2-carboxyanilinum bromide and chloride were analyzed and helpful in elucidating certain structural and bonding features. The asymmetric unit of the 2-carboxyanilinium cation with a protonated amino group, a bromide, chloride anion and a hydrogen-bonded lattice water molecule. Factor group analysis was also carried out.

EXPERIMENTAL SECTION

Crystals of the title compounds were obtained by crystallization from an aqueous solution of 2-aminobenzoic acid (anthranilic acid) with hydrobromic acid and hydrochloric acid respectively in a stoichiometric ratio of 1:1 by the slow evaporation method at room temperature. After a week period, small, needle-shaped crystals of 2-carboxyanilinium bromide monohydrate and 2-carboxyanilinium chloride monohydrate were obtained. Infrared spectral measurements were made with a Nexus 670 FTIR spectrometer with a resolution of ~1-2 cm^{-1} over the range 4000 – 400 cm^{-1}. The samples being mixed with KBr powder and pressed into discs under high pressure. The disc was transparent and yielded good spectra. Raman spectral measurements were made with a Nexus 670 FT-Raman spectrometer. Laser radiation of 633 nm was used as the source of excitation. A suitable notch filter placed before the monochromator suppressed the Rayleigh line. The laser power was maintained at 90mW. The measured spectral lines had a resolution of ~2-3 cm^{-1}. TGA/DTA analysis were carried out using the SII(SEIKO), Japan Analytical Instrument, Model No:TG/DTA-6500 with N_2 Atmosphere of range 20°C/Min.

RESULTS AND DISCUSSION

3.1. Crystal structure and factor group analysis

The unit cell of the crystal is determined using Bruker SMART APEX CCD area-detector diffractometer. The unit cell has four formula units (Z = 8). The crystallographic data collected for the grown crystals are reported in Table 1. The crystal structure and information about the hydrogen bonds were already reported in x-ray diffraction study [13,14].

Table 1: Crystallographic Data

Particulars	2 Carboxyanilinium Bromide Monohydrate	2 Carboxyanilinium Chloride Monohydrate
Molecular Formula	$C_7H_8NO_2^+.Br^-.H_2O^-$	$C_7H_8NO_2O^+.Cl^-.H_2O$
Molecular weight	236.07	191.61
Unit cell dimensions	a = 23.515(2) Å	a = 23.094(4) Å
	b = 4.8923(4) Å	b = 4.7833(8) Å
	c = 16.5222(12) Å	c = 16.381(3) Å
	β = 91.569(5)°	β = 91.605(9)°
Volume	1900.0(3)$Å^3$	1808.8(5)$Å^3$
Crystal system	monoclinic	Monoclinic
Space group	C2/c	C2/c
Z, Density	8, 1.650 Mgm^{-3}	8, 1.407 Mgm^{-3}

3.1.1. Factor Group Analysis

Factor group analysis is a method used for determining symmetry of vibrations. The numbers of normal modes of the crystals 2-Carboxyanilinium bromide and 2-Carboxyanilinium chloride were determined by group theory analysis using the correlation method based upon the symmetry of the molecules. The results obtained are presented in the Table 2. Factor group analysis using the standard correlation method was carried out [15,16]. There are 369 vibrational modes excluding the three acoustic modes ($\Gamma_{\text{acoustic}} = A_u^{IR} + 2B_u^{IR}$). It is distributed as $\Gamma_{crystal} = 93A_g^{IR,R} + 93B_g^{IR,R} + 92A_u^{IR} + 91B_u^{IR}$. The A_g and B_g species are IR and Raman active. The other two vibrational species A_u and B_u are only Raman active. The molecular configuration of the title compound is show in Figure 1.

Figure 1: Scheme diagram of 2 Carboxyanilinium Bromide and Chloride

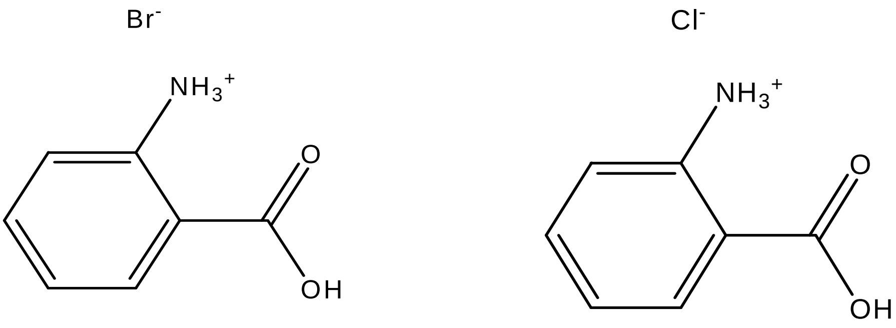


Table 2: Factor group analysis of 2 - Carboxyanilinium Bromide $C_7H_8NO_2^+.Br^-.H_2O$ and 2 - Carboxyanilinium Bromide $C_7H_8NO_2^+.Cl^-.H_2O$, space group: C2/c = C_{2h}; $z^b = 8$

	Modes and degrees of freedom for each species		Site symmetry C_1	Factor group analysis C_{2h}
Carboxyanilinium $C_7H_8NO_2^+$	Vibrational	384	A	$48A_g+48B_g+48A_u+48B_u$
Bromide/Chloride Br^-/ Cl^-	Vibrational	24	A	$3A_g+3B_g+3A_u+3B_u$
	Translational	24	A	$3A_g+3B_g+3A_u+3B_u$
	Libration	24	A	$3A_g+3B_g+3A_u+3B_u$
H_2O	Vibrational	24	A	$3A_g+3B_g+3A_u+3B_u$
	Translational	24	A	$3A_g+3B_g+3A_u+3B_u$
	Libration	24	A	$3A_g+3B_g+3A_u+3B_u$

$$\Gamma_{\text{vibrational}} = 54A_g^{IR,R} + 54B_g^{IR,R} + 54A_u^{IR} + 54B_u^{IR};\ \Gamma_{\text{translational}} = 6A_g^{IR,R} + 6B_g^{IR,R} + 6A_u^{IR} + 6B_u^{IR};$$

$$\Gamma_{\text{libration}} = 6A_g^{IR,R} + 6B_g^{IR,R} + 6A_u^{IR} + 6B_u^{IR};\ \Gamma_{crystal}^{total} = 66A_g^{IR,R} + 66B_g^{IR,R} + 66A_u^{IR} + 66B_u^{IR};$$

$$\Gamma_{\text{acoustic}} = A_u^{IR} + 2B_u^{IR};\ \Gamma_{crystal}^{optical} = \Gamma_{crystal}^{total} - \Gamma_{acoustic} = 66A_g^{IR,R} + 66B_g^{IR,R} + 65A_u^{IR} + 64B_u^{IR}$$

3.2. Vibrations of C-NH_3^+ group in Bromide, Chloride.

The FTIR and Raman spectrum of bromide compouond is given in Fig. 2 and Fig. 3 respectively. Similarly the FTIR and Raman spectrum of chloride compound is given in Fig. 4 and Fig. 5 respectively. The IR and Raman assignments are given in Table 3. The NH_3^+ group, which forms a part of the crystal, has C_{3v} symmetry in the free state with a pyramidal structure. Its normal modes of vibrations are $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(E)$, $\nu_4(E)$. Among these vibrations, the symmetry stretching and bending modes (ν_1 and ν_2) are non degenerate whereas the asymmetry stretching and bending modes (ν_3 and ν_4) are doubly degenerate [17]. All the modes are both IR and Raman active. The symmetry of the amino group may be lowered, thereby causing the shift in the vibrational wave numbers as the NH_3^+ group is attached to the rest of the molecule through hydrogen bonding. For the NH_3^+ group, the asymmetric and symmetric stretching modes are expected in the region 3150- 3000 cm^{-1}whereas the asymmetric and symmetric deformation modes of this group appear in the region 1660-1610 cm^{-1} and 1550-1480 cm^{-1} respectively [18]. The NH_3^+ symmetric stretching frequency is observed in both Br, Cl 3037, 3059 cm^{-1} in IR spectrum as a strong band. The NH_3^+ symmetric stretching frequency is observed both Br, Cl in the 2989 cm^{-1} in Raman spectrum as a strong band. As all the three NH bonds of the amino group take part in intermolecular hydrogen bonding the wave numbers of the stretching vibration of the NH_3^+ group is lowered. The NH_3^+ symmetric deformation mode occurs at 1621, 1626 cm^{-1} as very strong in IR spectrum whereas 1624 cm^{-1} as a very strong peak in the Raman spectrum. The NH_3^+ rocking mode is also observed at 1163 cm^{-1} as a medium band in the IR spectrum and 1186,1164cm^{-1} as medium band in Raman spectrum. The torsion mode is observed at 759,762 cm^{-1} as a medium and weak band in the IR spectrum and the wave number of 774,774 cm^{-1} in Raman spectrum is observed as a medium band. The torsion mode of C–NH_3^+ group is also identified and assigned [19].

Figure 2: FTIR spectrum of 2 Carboxyanilinium Bromide

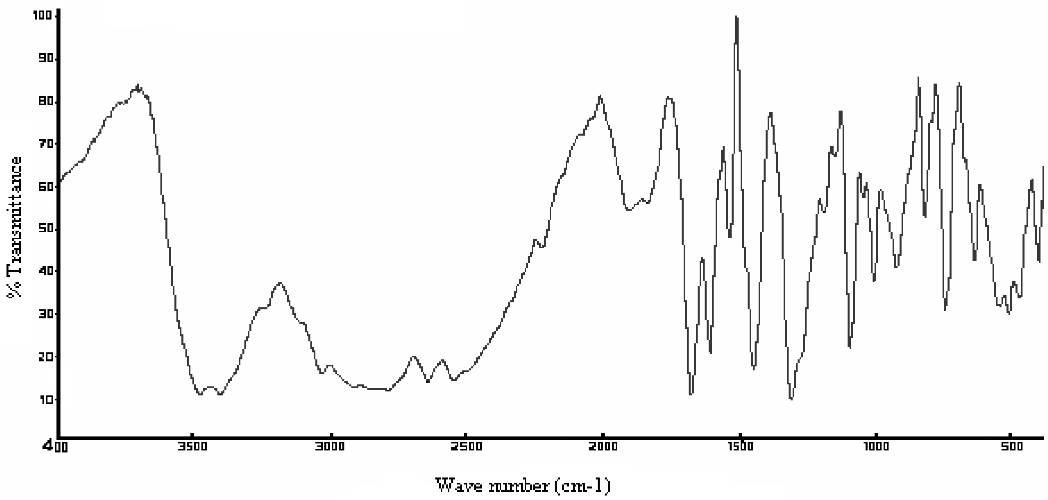


Figure 3: Raman spectrum of 2 Carboxyanilinium Bromide

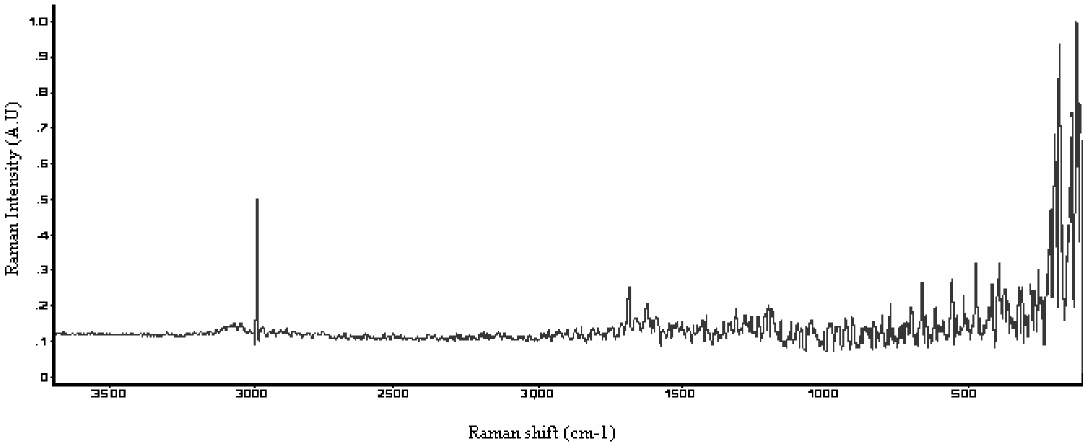


Figure 4: FTIR spectrum of 2 Carboxyanilinium Chloride

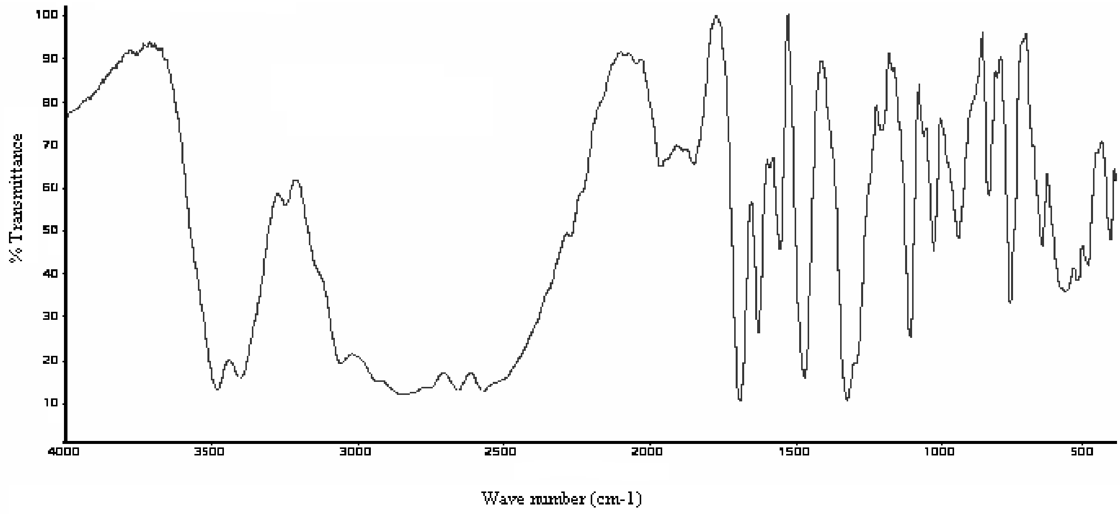


Figure 5: Raman spectrum of 2 Carboxyanilinium Chloride

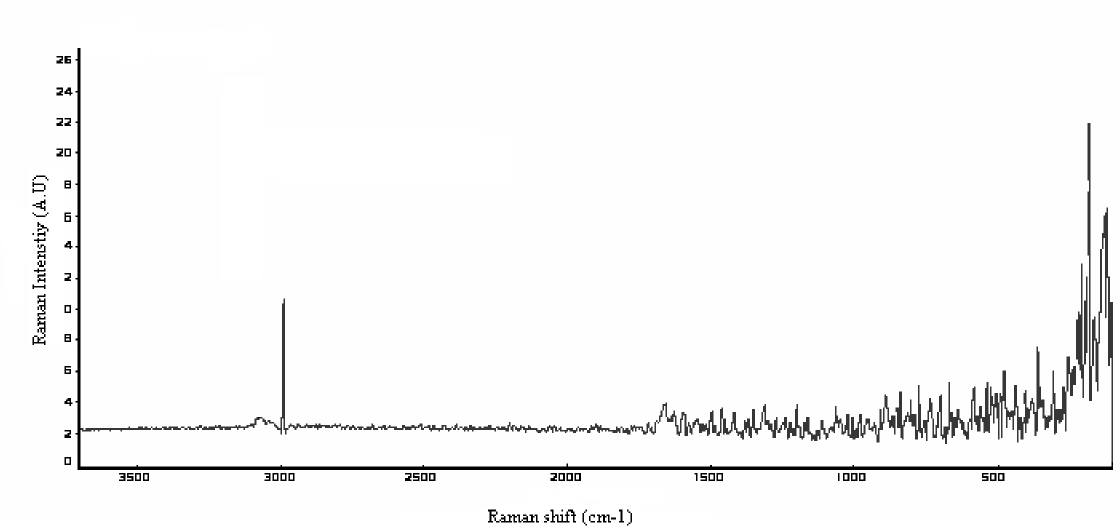


Table 3: FTIR and Raman assignments

2 Carboxyanilinium Bromide		2 Carboxyanilinium Chloride		Assignments
Infrared υ / cm^{-1}	*Raman υ / cm^{-1}*	*Infrared υ / cm^{-2}*	*Raman υ / cm^{-1}*	
		3754_{w}		O-H str., N-H…O str..
		3708_{vs}		O-H Str.H_2O trace
3484_{vs}		3483_{vs}		O-H Str.
3410_{s}		3410_{s}		O-H Str.
		3250_{vs}		O-H str., N-H…O str..
3037_{s}		3059_{s}	3077_{s}	O-H str.,C-H str, $[NH_3]^+$ sym. str.
	2988_{s}		2988_{s}	$[NH_3]^+$ asym. str.
2798_{s}		2847_{s}		O–H & C–O(H) str., O-H...O band
2651_{s}		2660_{s}		
$2557_{s}2235_{s}$		2570_{s}		
1917_{m}		2046_{m},1961_{m}		Overtones and combination bands
1846_{m}		1851_{m}		
1687_{s}	1687_{s}	1690_{s}	1659_{s}	C=O Str.
1621_{m}	1624_{m}	1626_{m}		$[NH_3]^+$ asym. def., φ quad. ring
		1588_{s}	1595_{s}	COO^- asym. str., NH_3^+ asym. def.
1548_{m}		1554_{m}	1552_{m}	COO^- asym. str., NH_3^+ asym. def.
	1500_{m}		1499_{m}	COO^- asym. str., NH_3^+ asym. def.
1460_{s}		1469_{s}	1450_{s}	C-N asym. str.
	1430s			OH i.p def
	1415s		1417s	OH i.p def
		1367s,1351s		C-N sym str
1324_{vs}		1326_{vs}		-OH i.p. def.
	1313_{m}		1314_{m}	C=O
	1235_{sh}		$1239,1224_{sh}$	-OH i.p def
1202_{var}	1999_{var}	1203_{var}	1202_{var}	-OH
1163	1186		1164	-OH,$[NH_3]^+$ rocking
1108_{s}	$1119,1097_{s}$	1108_{s}	1113_{s}	C-O str
1057_{s}	1050_{s}	1059_{s}	1067_{s}	C-O str
1019_{s}		1024_{s}	$1021,1004_{s}$	C-O str
	988		979	O-H o.p def
937	950,931	941	956	O-H o.p def
	906		908	$[NH_3]^+$ rocking, C-C str. $[NH_3]^+$ rocking, o.p. C–H (ring)
833	864,828		890,868,852,840	$[NH_3]^+$ rocking, C-C str. $[NH_3]^+$ rocking, o.p. C–H (ring)
	800	806	802	C-H o.p def
759	773	762	792,774,757,737	wag.; φ o.p. C–H def. C-O-H torsion
	702		703	
653	661,646,615	654	688,674,663	O–C = O i.p. def.;
560_{m}	557_{m}	572_{m}	582_{m},559_{m}	COO^- wag., H_2O wag., NH_3^+ tor.
526_{m}	514_{m}	532_{m}	538_{m},522_{m},505_{m}	O-H str
488_{m}	474_{m}	497_{m}	477_{m},452_{m},437_{m}	NH_3^+ torsion COO^- rock
416_{m}	417_{m}		421_{m},407_{m}	φ i.p quad. Ring def
	393_{w},372_{w},361_{w}		381_{w},362_{w},352_{w}	C-C-C-C o.ph. def.
	323_{w},312_{w},299_{w}		335_{w},324_{w},309_{w}	C-C-C-C o.ph. def.
	282_{w},266_{w},250_{w}, 241_{w}		294_{w},282_{w},268_{w},251_{w}	Lattice vibration modes
	210_{w},197_{w}		233_{w},216_{w},205_{w},192_{w}	
	180_{w},170_{w},149_{w},138_{w}, 120_{w}		181_{w},161_{w},129_{w},118_{w},103_{w}	

3.3. Vibration of O-C=O,C-C=O group

The α branched aliphatic monocarboxylic acids generally exhibit three strong bands due to in plane vibration of the O-C=O group, at 655,635,620 cm^{-1} which are not resolved in the region 665-610 cm^{-1}[15]. The stretching vibration of the C=O bond is a non ionized carboxylic (COOH) group usually appear in the wave number 1755-1700 cm^{-1}. For the title compounds, the C=O is identified as very strong intensity lines at 1687,1690 cm^{-1} in IR spectrum and 1687,1659 cm^{-1} in Raman spectrum. The strong band is found at 555-520 cm^{-1} which is attributed to the in-plane Vibration of the C-C=O group [15]. The medium band at 653,654 cm^{-1} in the IR Spectrum and the corresponding medium Raman spectrum at 661, 668 cm^{-1} are due to the in-plane deformation mode of C-C=O group.

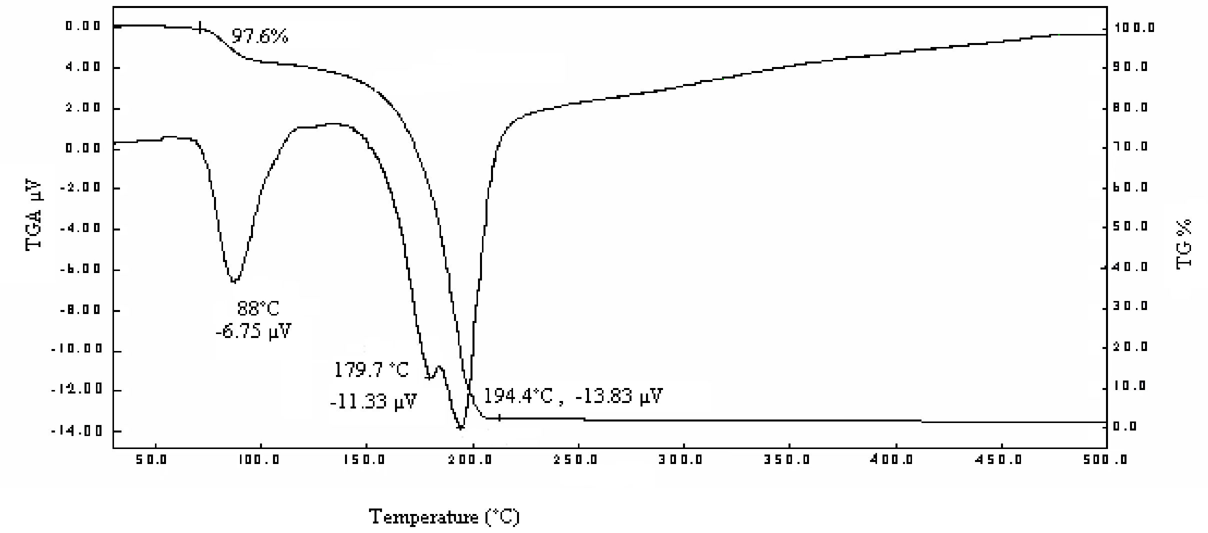
3.4. Vibration of OH group

The OH stretching of wave number in the carboxylic group of 3410 cm^{-1} is appeared in very strong band in both IR Spectrum of title compounds. A broad and strong intensity band at 3037 ,3059 cm^{-1}in IR and 3077 cm^{-1} in Raman assigned to O-H stretching. The O-H stretching in the lower band is observed in the frequencies at 937, 941 cm^{-1} and 950, 956 cm^{-1} as a medium band in both IR and Raman spectrum are due to out of plane deformation.

3.5. Hydrogen Bonding

Hydrogen bonds are very important for dipole interactions in stabilizing the protein structures. The amino acids having zwitterionic form $[NH_3]^+$ moiety are a good donor and carboxylate group is an excellent acceptor. In biological crystals, hydrogen bonds link the adjacent molecules, where O-H-O hydrogen bonds are relatively stronger than N-H---O bonds. These hydrogen bonding give the structure cohesion in three dimensions, its effect is very important in a crystal. It will cause a down shifting of stretching vibrational modes and up shifting of deformation modes. Normally in amino acids, strong hydrogen bonds are formed between protonated amino group and carboxyl group. In the present structure, the over all analysis reveals that both amino and carboxyl group residues exhibit similar hydrogen bonding features.All ammonium H atoms are involved in hydrogen bonds with two different bromide anions and the third with the carbonyl O atom of the same molecule. A strong intra molecular N—H···O hydrogen bond is a characteristic feature in many anthranilic acid complexes. The main intermolecular interactions are of the N—H----O/Br and O—H----O/Br types [6,7]

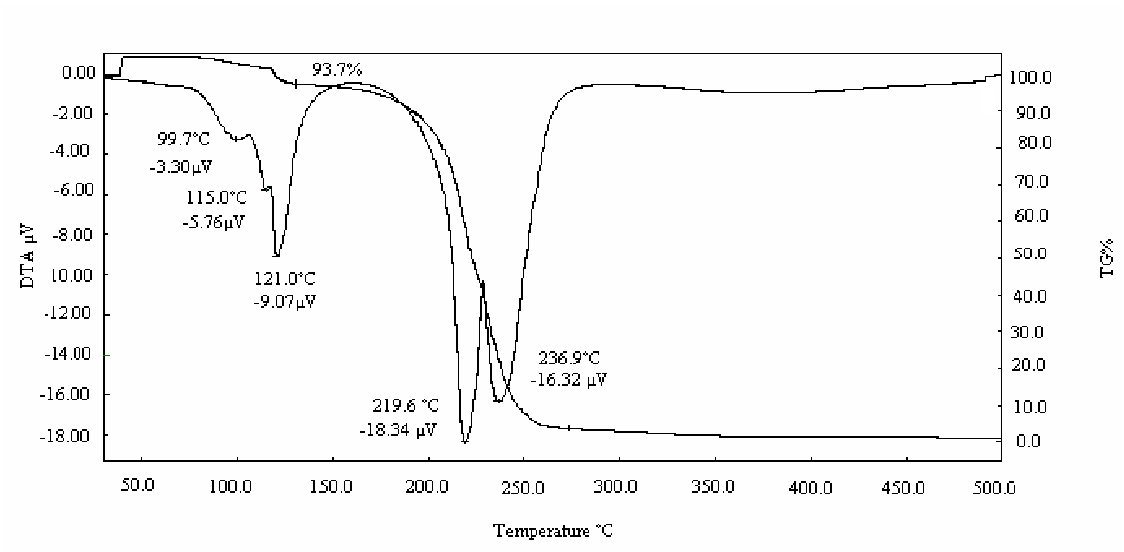
Figure 6: TGA/DTA Curve of 2 Carboxyanilinium Bromide



3.6. Thermal Analysis

The TGA curve of the title compounds (Fig. 6 and Fig. 7) shows the decomposition percentage of title compounds at various temperatures. Apparently, there is no phase change between room temperature and 194°C for 2carboxyaniliuinm chloride, but the material starts to decompose above 194°C and similarly for 2carboxyanilinium bromide the material start decompose above 236°C. In both the crystals, a small weight loss near to 100° C is appeared in TGA indicate the liberation of water of crystallization. The major peak is the melting point of the crystal as the major weight loss occurs after that point and the minor peak is assumed to be a weak solid to solid phase transition. The DTA curve presents several endothermic or exothermic peaks due to the decomposition and elimination of volatile pyrolysis products.

Figure 7: TGA/DTA Curve of 2 Carboxyanilinium Chloride



CONCLUSION

The IR and Raman have been assigned for 2 carboxyanilinium complexes. The present study was undertaken on the isomorphous bromide, chloride salts of 2-aminobenzoic acid to investigate their hydrogen-bonding interactions, aggregation patterns and crystalline packing of the molecules. The stretching wave numbers of hydroxyl group deviate very much from their positions owing to strong hydrogen bond existing between the carboxyl group and bromide, chloride anion. Anthranilic acid occurs as zwitterion, depending on the environment and pH of the solution. The downshifting of the wave numbers of some stretching modes and the corresponding increase in the wave numbers of the bending modes of vibration indicates represents of extensive intermolecular hydrogen bonding between carboxyl group and uncoordinated water molecule.

Acknowledgement

SAB sincerely thank the Vice-Chancellor and Management of the Kalasalingam University, Anand Nagar, Krishnan Koil -626 126, for their support and encouragement. SA thanks the Vice Chancellor of Anna University of Technology for his support and encouragement.

REFERENCES

[1]The Merck Index, 13th ed.; Merck Research Laboratories: Whitehouse Station, NJ, **2001**, 74.
[2]ST Dhume; MB Ebert; GN Saddic; KR Anumula. *Met. Mol. Biol*., **2002**,194**,**127.
[3]P Wiklund; J Bergman. *Curr. Org. Syn*., **2006**, 3, 379-402.
[4] J Reiter; A Beyer; M Potschka; P Schuster. *J. Phys. Chem*., **1989**, 93, 442-451.
[5]RH Prager; GR Skurray. *Aust. J. Chem*., **1968**, 21, 1037.
[6]K R Anumula. *Glycobiology*, **1993**, 3, 511.
[7]KR Anumula. *Anal. Biochem* ., **1994**, 220**,** 275.
[8]CJ Brown. *Proc. Roy. Soc. A*.. **1968**, 302, 185-199.
[9]Bellamy Lj, The Infrared spectra of complex molecules. Wiley: New york **1975**
[10]Y In; H Nagata; M Doi; T Ishida; A Wakahara. *Acta Cryst.*, **1997**, C53, 646-648.
[11]AF Borowski; DJ Cole-Hamilton. *Polyhedron*, **1993**, 12, 1757.
[12]T Huey Lu; P hattopadhyay; FL Liao; J Mau Lo. *J.Analytical sciences*, **2001**,17, 905-906.
[13]SARA Zaidi; MN Tahir; J Iqbal; MA Chaudhary. *Acta Cryst*,, **2008**, E64, 1957.
[14]V Susindran; S Athimoolam; SA Bahadur; B Sridhar. *Acta Cryst*., **2009,** E65,3247.
[15]G Socrates. Infrared Characteristic Group Frequencies. Wiley: New York, **1980**.
[16]AL Spek. *Acta Cryst*., **2009**, D65, 148.

---

[17]CF Macrae; PR Edgington; P McCabe; E Pidcock; GP Shields; R Taylor; M Towler; J van de Streek. *J. Appl. Cryst.*, **2006**, 39, 453.
[18]I Hubert Joe; D Philip; G Auraldas; IL Botto. *J.Raman Spectrosc*., **1991**,22 ,423.
[19]K Nakamoto. Infrared and Raman spectra of inorganic and coordination compounds: Part A: theory and applicatios in inorganic chemistry, New York: Wiley-interscience, **1997**5 ed.,**.**