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Fourier Transform Infrared Ab Initio And PM3 Calculations For Some Carboxylic Acids

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Abstract

Fourier Transform Infrared of three carboxylic acids adipic, cinamic and hippuric acids as microcrystalline powder have been studied. The vibrational spectra were calculated using PM3 and ab initio calculations employing the poluk ribiere optimizer for cinamic and hippuric acids while the steepest descent optimizer was used for adipic acid. It was found that the remarkable differences concerning with the assignments of the vibrational spectra which were investigated between PM3 and ab initio methods. In addition the calculated spectra were compared with experimental data.

اطياف تحويل فوريير تحت الحمراء لثلاثة أحماض كاربوكسيلية

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الخلاصة

تم في هذا البحث أستقصاء اطياف تحويل فوريير تحت الحمراء لثلاثة أحماض كاربوكسيلية كمسحوق بلوري دقيق :وهي أحماض الادبيك ,السيناميك والهيبارك .حسبت الاطياف الاهتزازية باستخدام حسابات ab initio وPM3 (عند المستوى الاوطأ STO-3Q) بتوظيف الموائم polak ribiere ماعدا حامض الادبيك فقد استخدم الموائم steepest descent .في الحسابات لوحظت فروق ترتبط بألاطياف الاهتزازية مابين الطريقتين ab initio وPM3 .لقد قورنت الاطياف المحسوبة مع الاطياف العملية.

Introduction

Hippuric acid is naturally occurred as amino acid analogue. It is an *N*-benzoyl derivatives of glucine and may be considered as similar to *N*-acetylglycine but with the methyl group replaced with a phenyl group. From radiation chemical point of view it is interested to investigate the effect of an aromatic phenyl substitution on the primary radiation processes of the peptide bond [1]. The study of the reaction between metals and hippuric acid or 4- amino hippuric acid is become as an interest topic due to their presence in biological system. It is produced in the renal metabolism of *p*-amino benzoic acid and it is also in evolved in sulfate to transport in human neutrophils [2-4]. The synthesis and characterization of bivalent, trivalent and mixed ligand transition and lanthanides metal complexes of hippuric acid have been reported [5-13]. The dissociation constants of hippuric acid as well as the stability constant of its bivalent and trivalent metal ion complexes in different mixed aqueous organic solvent at different temperatures have been calculated using potentiometric studies [14]. The production of trans-cinamic acid from various alkyl benzene by micro organics was intensively studied by use of aco-oxidation technique [15]. Both film and danckwerts theories have been applied to study the ozonation kinetics of cinamic acid and ortho-hydroxy cinamic acids, where the one carbon- carbon double bond and the aromatic ring with a hydroxyl group are very reactive toward ozone[16]. 3-chloro carbonyl benzo-b-thiophene was prepared from cinamic acid and then converted by three routes to important compounds: oxadiazoles, thiazoles and triazoles [17]. Some an infertile inhibitors of 18 to 24-memberd tetra azamacrocyclic complexes of iron (ll) and manganese (ll) have been synthesized by condensation reaction using 1, 3-phenylenediamine with malonic acid, succinic acid, glutaric acid and adipic acid [18]. The synthesis of two new families of dendrimers based on the esterification of *N*-alkylated-3-amine-1-propanol with two different cores of adipic acid and ethylene diamine was considered as flexible non-cytotoxic nano carries of poorly water-soluble drugs such as methotrexate and wrdely which have been used in chemotherapy [19]. In this work we try to carry out ad failed analysis of theoretical vibrational spectra of these three acids by using means PM3 and ab initio calculations employing the poluk ribiere optimizer except for adipic acid the steepest descent optimizer was used.

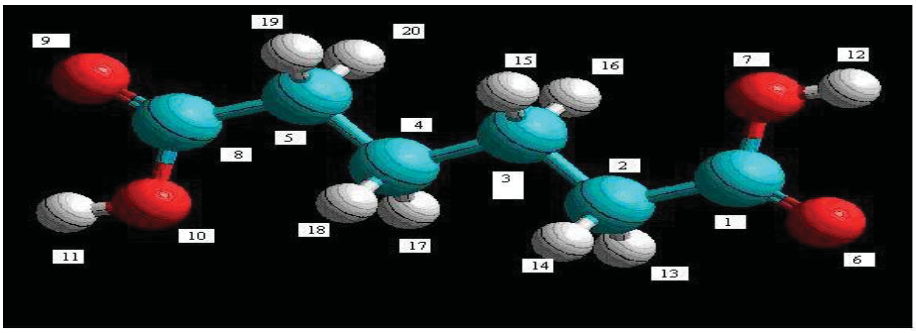
Experimental

All of the carboxylic acids in this investigation are analytical grade. The experimental FT-IR spectra of carboxylic acids were recorded on ashimadzo FT-IR spectrometer using KBr pellets at room temperature in the spectral range of 4000-200 cm^{-1}. Data were collected with a resolution of 4 cm^{-1}. The scanning speed was held at.

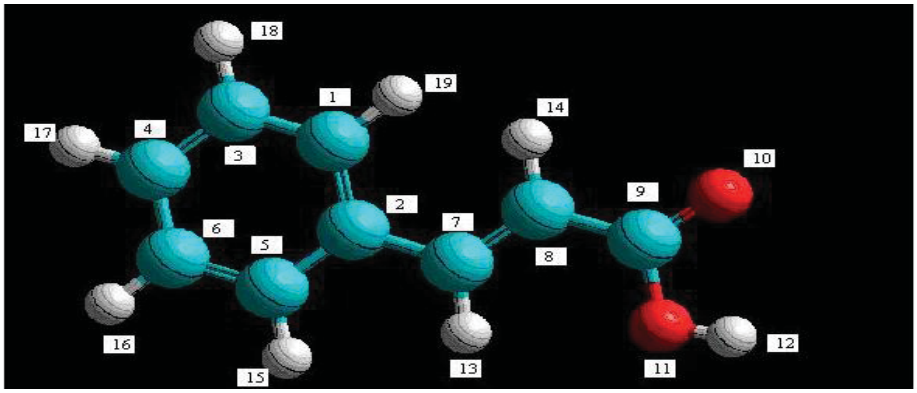
Computational methods

All calculations were carried out using the Hyperchem 8.02 suite of Quntum Chemistry/Molecular Mechanics, programs with standard parameters [20]. Running on windows Xp platform 2GHz Intel Pentium IV cpu-personal computer. To save computational time, initial optimization were carried out with the Molecular Mechanics (MM) methods using the AMBER force fields. The lowest energy conformations of the molecules obtained by the MM method which were further optimized by PM3 and ab initio (at minimal (S TO-3G) level) calculations [21]. Employing of the poluk ribiere optimizer except for adipic acid, the steepest descent optimizer was used. In this work, the calculated geometry using the semi-empirical and ab initio methods was considered only the gas phase, where the molecule is free of interaction. So it was expected to find some differences with experimental structure of the solid state[22]. The vibrational spectra were subsequently calculated with the same methods and levels.

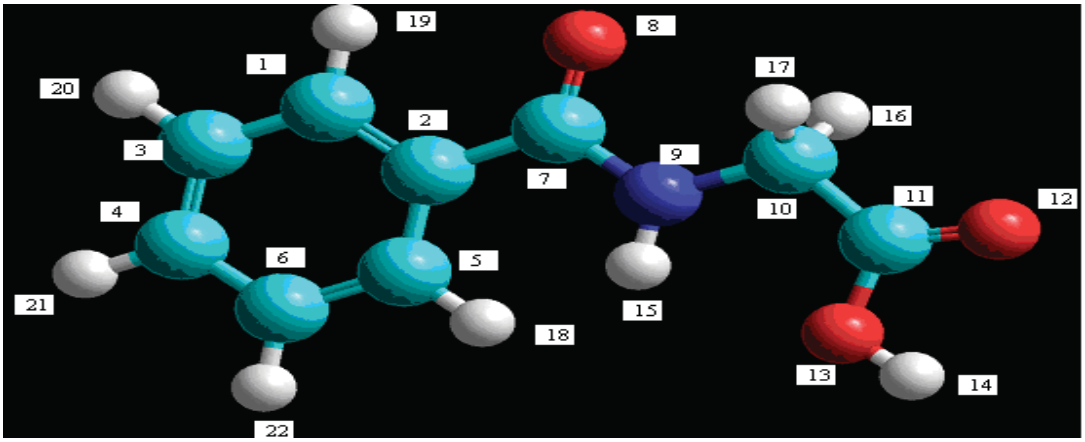
Results



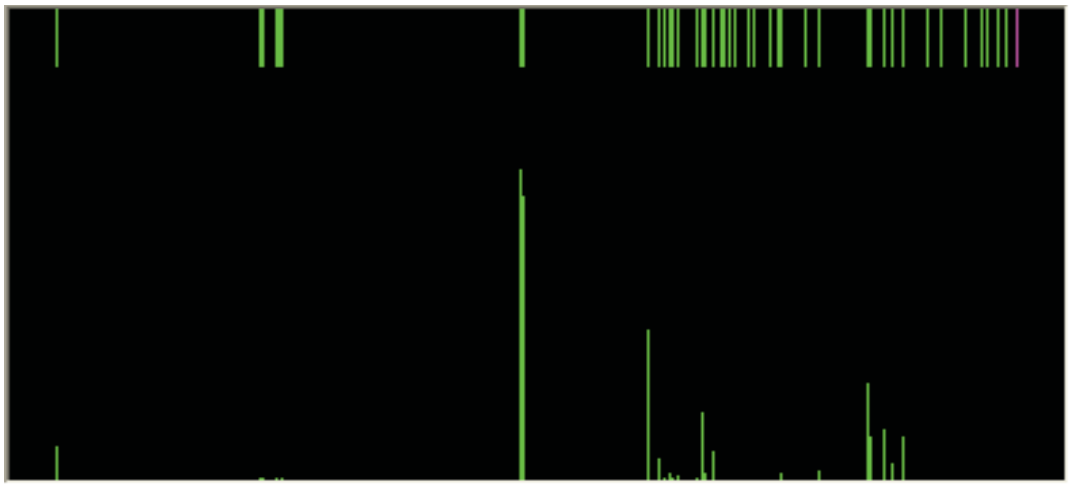
Figure(1): The PM3 calculated structure of adipic acid



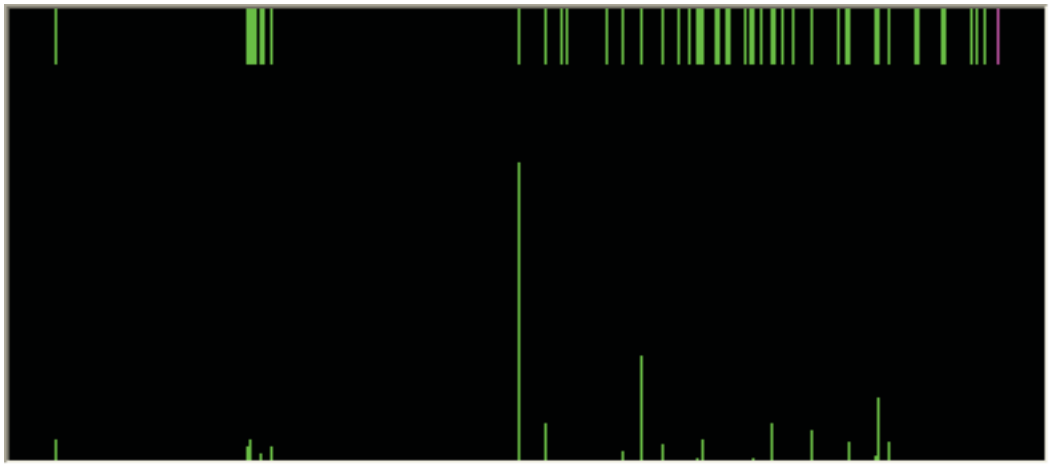
Figure(2): The PM3 calculated structure of cinamic acid



Figure(3): The PM3 calculated structure of hippuric acid



Fig(4) FT- IR of compound adipic acid



Fig(5) FT- IR of compound trans-cinamic acid

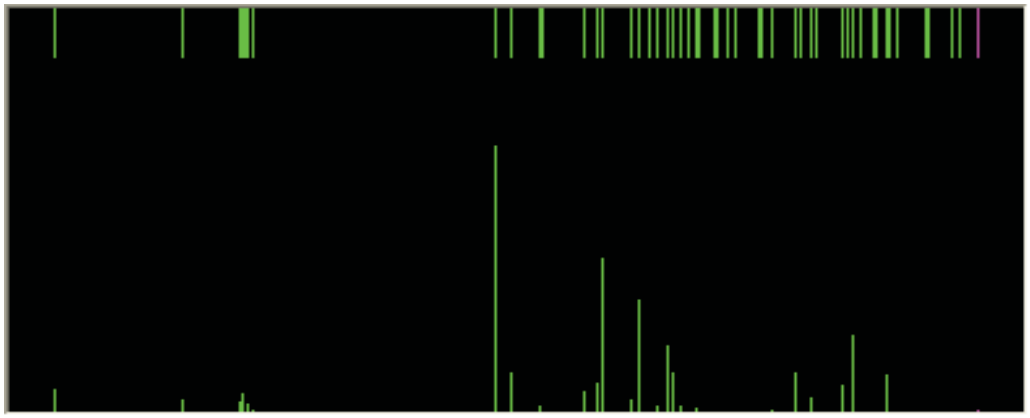
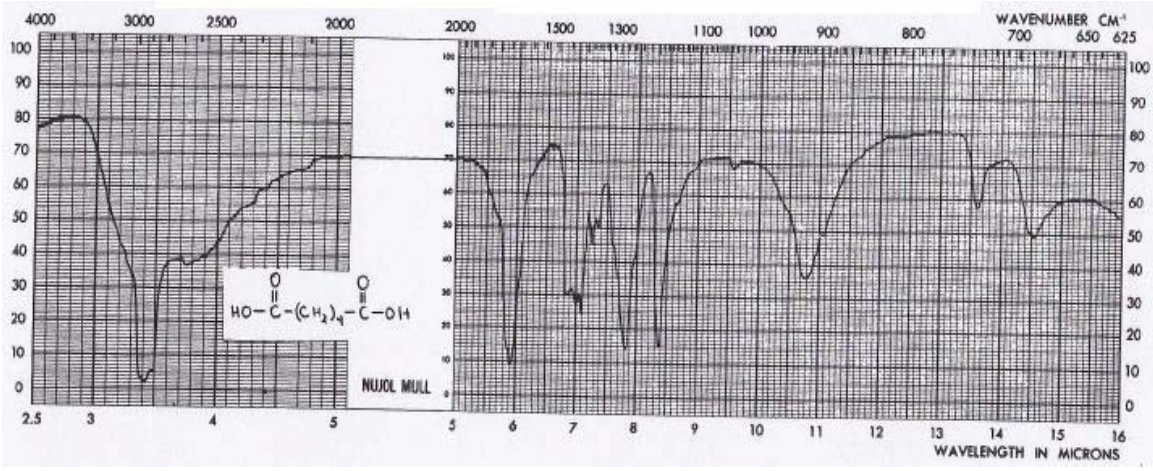
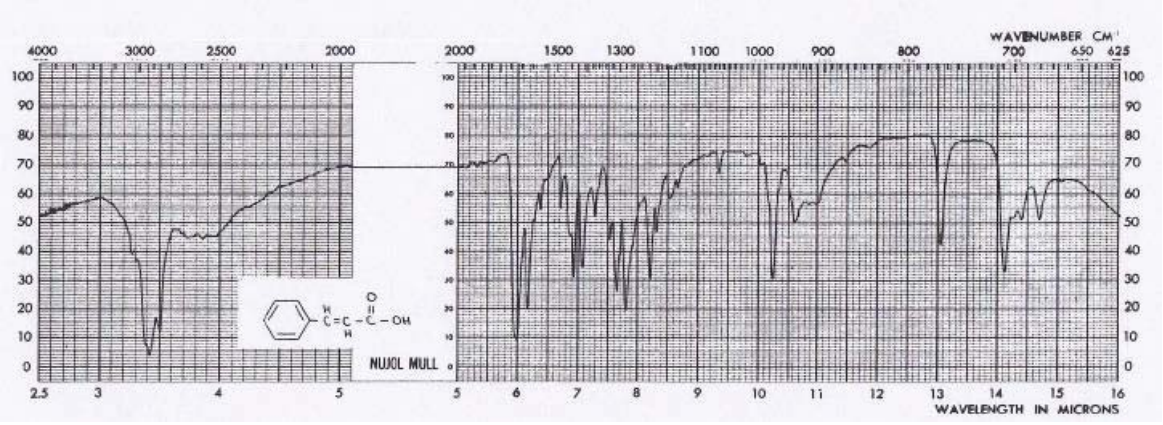


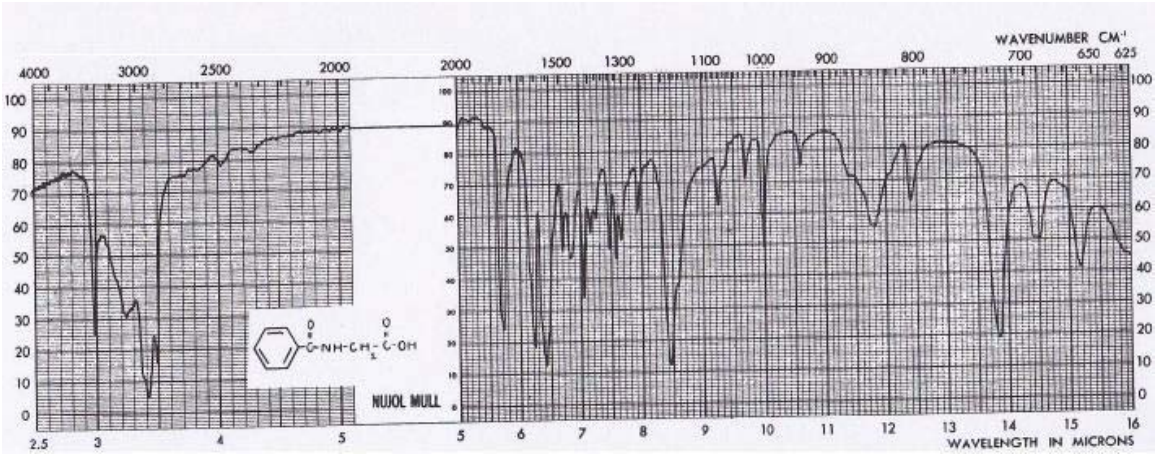
Fig (6) FT- IR of compound hippuric acid



Fig(7) FT- IR of compound adipic acid



Fig(8) FT- IR of compound trans-cinamic acid



Fig(9) FT- IR of compound hippuric acid

Table (1): PM_3 calculated IR spectra data of adipic acid.

Frequency,cm^{-1}	Intensity,$km.mol^{-1}$	Assignment
3852.94	0.15733	υ_s.O-H
3852.87	32.84261	υ_{as}.O-H
3035.26	1.42292	υ_s.C-H of $C_3H_{15}H_{16}$,and $C_4H_{17}H_{18}$
3033.11	0.00000	υ_s.C-H of $C_3H_{15}H_{16}$, $C_4H_{17}H_{18}$,and vw.υ_s. of other C-H
3023.62[a] 3023.34[a]	6.25015 0.00004	υ_s.C-H of C_5-H_{19}, $C_2H_{13}H_{14}$,and C_2-H_{13}
3023.34	0.00004	υ_s.C-H of $C_3H_{15}H_{16}$, $C_4H_{17}H_{18}$, and vw υ_s. of other C-H
2963.64 2942.30	2.82619 4.43457	υ_{as}.C-H of C_5-H_{19}, C_5-H_{20}, $C_2H_{13}H_{14}$, and vw υ_{as}. of other C-H
2954.46 2938.77	0.00000 0.00000	υ_{as}.C-H
1971.78	0.00001	υC=O[b]

1970.02	285.47389	υC=O[c]
1453.42	0.00002	υC-OH[b]
1451.33	145.53148	υC-OH[c]
1420.56	0.00000	υC-C of C2-C3,C3-C4 and υC-OH[b]
1414.25	0.00000	δ_s.CH_2 of $C_3H_{15}H_{16}$,$C_4H_{17}H_{18}$ and vw δ_s.CH_2 of other CH_2
1399.37	1.04344	δ_s. of $C_2H_{13}H_{14}$and $C_3H_{15}H_{16}$ opposite to[d] δ_s. of $C_4H_{17}H_{18}$ and $C_5H_{19}H_{20}$
1375.31	7.76991	δ_s. of $C_3H_{15}H_{16}$ and $C_5H_{19}H_{20}$ opposite to[d] δ_s. of $C_2H_{13}H_{14}$ and $C_4H_{17}H_{18}$
1362.36	0.00000	δ_s. of $C_2H_{13}H_{14}$ and $C_5H_{19}H_{20}$ opposite to[d] w δ_s. of $C_3H_{15}H_{16}$ and $C_4H_{17}H_{18}$
1345.87	5.83425	δ_s. of $C_2H_{13}H_{14}$ opposite to[d] δ_s. of $C_5H_{19}H_{20}$
1277.43	0.00000	ω CH_2 ,δ_s.O-H and wυC=O
1239.01	32.81833	δ_s.O-H[d] and vw ω CH_2 of $C_3H_{15}H_{16}$ and $C_4H_{17}H_{18}$
1227.11	0.00001	δ_s.O-H
1206.61	15.60630	δ_s.O-H[d] and ω CH_2
1161.97 1124.68 1053.92	0.00192 0.00000 0.94189	τ CH_2
1158.04	0.00000	τ CH_2 of $C_3H_{15}H_{16}$ and $C_4H_{17}H_{18}$ and wτ CH_2 of others

1137.90	0.00000	υC_3-C_4
1131.22	0.57557	$\upsilon_{as.}$C-C^e of C_2-C_3 and C_4-C_5
1113.51	0.00000	υ_sC-C of C_2-C_3, C_3-C_4 and C_4-C_5
1029.95 920.83 822.23 766.03	0.00000 4.34380 0.00000 5.83399	Out-of-plane bending of whole molecule except O-H
951.11	0.00000	$\upsilon_{s.}C_1$-C_2 and $\upsilon_{s.}C_5$-C_8
924.43	1.76083	υ_{as} C_1-C^e_2 and $\upsilon_{as.}C_5$-C_8
565.98	65.20659	Out-of-plane bending of COOH
563.93	0.00024	Out-of-plane bending of COOH and τ CH_2 of $C_2H_{13}H_{14}$ and $C_5H_{19}H_{20}$
538.68	5.91530	bending of C-C-C angle
512.14 449.88	0.00000 0.00001	δ_s of angle O=C-OH
502.79 502.12	48.88406 0.00296	Out-of-plane bending of O-H
453.82	38.74277	In plane bending of C=O
329.16	0.92559	$\upsilon_{as.}$O-H and skeletal vibrations
289.18 117.10 88.11 40.77 -33.29	0.00000 0.00000 0.90707 0.39947 0.00000	skeletal vibrations
180.17	0.00000	υ_a.O-H and skeletal vibrations

86.37	0.14266	skeletal vibrations except COOH
-23.08	2.29277	Out-of-plane bending of COOH

$\upsilon_{s.}$: Symmetrical stretching; $\upsilon_{as.}$: asymmetrical stretching ; vw $\upsilon_{s.}$: very weak symmetrical stretching ; a : two bands with different intensities but are assignmented to the same stretching vibration ; b : the two CO stretch in the same direction in plane ; c : the two CO stretch in opposite directions in plane ; $\delta_{s.}CH_2$: in-plane bending of CH_2 or scissoring ; d : while two CH2 (or OH) bend as closing of scissors , the two other CH2 bend as opening the scissors ; w$\upsilon_{s.}$: Weak scissoring; ω CH_2: out-of-plane bending of CH_2 or wagging; τ CH_2 out-of-plane bending of CH_2 or twisting; e: C-C bond stretches in opposite to stretching to other one

Table (2): Ab initio calculated IR spectra data of adipic acid.

Frequency,cm^{-1}	Intensity,$km.mol^{-1}$	Assignment
4251.18	0.00053	$\upsilon_{s.}$O-H
4250.85	19.70733	$\upsilon_{as.}$O-H
3737.27	2.31254	$\upsilon_{as.}$C-H of $C_3H_{15}H_{16}$, $C_4H_{17}H_{18}$, and vw$\upsilon_{as.}$ of other C-H
3728.03	0.00001	$\upsilon_{as.}$C-H of $C_3H_{15}H_{16}$, $C_4H_{17}H_{18}$, and w$\upsilon_{as.}$ of other C-H
3713.99	0.12811	$\upsilon_{as.}$C-H of $C_2H_{13}H_1$, $C_5H_{19}H_{20}$, and vw$\upsilon_{as.}$ of other C-H
3713.74	0.00016	$\upsilon_{as.}$C-H of $C_2H_{13}H_1$, $C_5H_{19}H_{20}$, and w$\upsilon_{as.}$ of other C-H
3617.92	3.07791	$\upsilon_{s.}$C-H of $C_3H_{15}H_{16}$, $C_4H_{17}H_{18}$, and

3615.89	0.00040	υ_s.C-H of $C_3H_{15}H_{16}$, $C_4H_{17}H_{18}$, and wυ_s. of other C-H
3606.50 3605.41	0.00011 1.30846	υ_s.C-H of $C_2H_{13}H_1$, $C_5H_{19}H_{20}$, and vwυ_s. of other C-H
2127.66	0.06577	υC=O[b]
2127.36	188.49870	υC=O[c]
1835.56	2.60557	δ_s.CH_2 of $C_3H_{15}H_{16}$,$C_4H_{17}H_{18}$ and v.wδ_s.CH_2 of other CH_2
1818.14	0.00002	δ_s.CH_2 of $C_3H_{15}H_{16}$,$C_4H_{17}H_{18}$ and wδ_s.CH_2 of other CH_2
1799.33	0.00008	δ_s.CH_2 of $C_2H_{13}H_1$, $C_5H_{19}H_{20}$, and wδ_s.CH_2 of other CH_2
1796.89	2.71203	δ_s.CH_2 of $C_2H_{13}H_1$, $C_5H_{19}H_{20}$, and vwδ_s.CH_2 of other CH_2
1734.18 1561.46	0.00000 0.00001	ω CH_2
1676.72	13.53600	ω CH_2 and δ_s.O-H[d]
1651.10	0.00000	δ_s.O-H
1637.62	41.83007	δ_s.O-H[d] and ω CH_2
1558.09	0.00000	τ CH_2 of $C_3H_{15}H_{16}$,$C_4H_{17}H_{18}$ and and vwτ CH_2 of others
1550.98 1360.76	0.21589 1.32284	τ CH_2

1497.46	0.00007	τ CH_2 of $C_2H_{13}H_1$, $C_5H_{19}H_{20}$, and ρ CH_2 of $C_3H_{15}H_{16}$,$C_4H_{17}H_{18}$
1477.92	71.41251	ω CH_2 and $\upsilon_{as.}$C-O
1435.33	0.00052	$\upsilon_{s.}$C-O and $\upsilon_{s.}$C-C of C_1-C_2 ,C_5-C_6
1416.55	258.13004	$\upsilon_{as.}$C-O , $\upsilon_{as.}$C-C of C_1-C_2 ,and C_5-C_6 ,and ω CH_2
1360.76 842.45	1.32284 8.64623	τ CH_2 and out –of-plane bend. of C=O
1294.24	0.00000	ρ CH_2 and out –of-plane bend. of C=O
1273.96	0.00000	$\upsilon_{s.}$C-C of C_2-C_3 ,and C_4-C_5
1237.42	0.00000	υ C_3-C_4
1234.52	0.64889	$\upsilon_{as.}$C-C of C_2-C_3 ,and C_4-C_5
1070.72	5.61179	ρ CH_2 of $C_2H_{13}H_1$, $C_5H_{19}H_{20}$, τ CH_2 of $C_3H_{15}H_{16}$,$C_4H_{17}H_{18}$ and out –of-plane bend. of C=O
984.34	0.00000	$\upsilon_{s.}$C-O and $\upsilon_{s.}$C-C of C_1-C_2 , C_5-C_6
962.82	4.10036	$\upsilon_{as.}$C-O and $\upsilon_{as.}$C-C of C_1-C_2 , C_5-C_6
914.38	0.00002	ρ CH_2 and out –of-plane bend. of C=O
633.08	60.92858	$\delta_{s.}$of angle O=C-OH
631.25	131.20366	Symm.out-of-plane bending of COOH
629.85	0.00386	out-of-plane bending of CO and OH

ρ	624.64	0.00053	δ_s.of angle O=C-OH
: in-	550.04	0.01393	out-of-plane bending of OH
	549.94	64.97774	out-of-plane bending of COOH
	542.13	36.90201	In-plane bend. of C=O
	526.42 306.81	0.00003 0.00000	in-plane bending of whole molecule
	344.98 83.53	1.50264 0.32489	υ_{as}.OH and in-plane bending of whole molecule
	179.35	0.00000	υ_s.OH and in-plane bending of whole molecule
	135.83 112.17 45.57 -56.92	0.00000 0.03503 0.19939 0.00000	out-of-plane bending of molecule
	-37.01	1.32161	out-of-plane bending of COOH

CH_2 plane bending of CH_2 or rocking

Table (3):PM_3 calculated IR spectra data of cinamic acid.

Frequency,cm^{-1}	**Intensity,$km.mol^{-1}$**	**Assignment**
3855.14	**19.86674**	**υO-H**
3077.83	**13.20415**	**υ_s.ar.C-H**
3067.07 **3057.57** **3050.55**	**20.03639** **3.23128** **2.60198**	**υ_{as}.ar.C-H**
3025.46	**7.75207**	**υ C_7-H_{13}**
3010.96 **2977.95**	**2.77947** **14.42232**	**υ ar.C-H and υ C_8-H_{13}**
1975.46	**235.74655**	**υ C=O**
1856.90	**31.75677**	**υ C_7=C_8 and wυ C=O**
1795.71	**3.32999**	**υar. C=C**

1776.95 1543.56	0.64331 9.65117	
1608.04	1.23679	ʋar. C=C and ʋ C_2-C_7
1469.64	85.61916	ʋ C-O
1389.15	14.81324	ʋ C_2-C_7, In plane bending of ring, and vwʋ C-O
1325.18	1.31217	ʋar.C-C and in-plane ole.C-H bend.
1284.50	0.76416	In-plane bend.C_8-H_{14}, ar. C-H bend. and vw. bend. of O-H
1246.78	4.73266	In-plane bend.C_7-H_{14}, ar. C-H bend. and bend. of O-H
1234.63 1167.19	0.90298 1.46094	In-plane bend. of C_7-H_{14}, C_8-H_{14}, ar. C-H bend. and wbend. of O-H
1219.12	19.83979	In-plane bend. of C_7-H_{14}, C_8-H_{13}, vw ar. C-H bend. and bend. of O-H
1153.08	0.04684	In-plane bend. of ar. C-H
1128.78	1.29650	ʋ C_2-C_7, In plane bending of ring
1110.63	0.07060	In-plane bend. of ar. C-H and vw C_8-H_{14}
1054.05	0.80073	In plane bending of ring ,ʋ C_2-C_7, ʋ C_8-C_9, and vw ʋC-O
1025.02 988.81 982.37 773.44	0.00035 0.44506 0.00921 26.39837	Out-of- plane bending of molecule except OH
1013.73	5.33894	ʋC-O and ʋC_8-C_9
937.33 925.72	32.00274 0.06408	Out-of- plane bending of C-H and C=O
900.81 633.38	0.53116 0.33116	In plane bending of ring

851.41	0.23906	Out-of- plane bending of ar.C-H
664.88	0.93042	Out-of- plane bending of molecule except H_{13}-C=C-H_{14}
626.00 460.91 231.35 69.31	16.38738 0.24510 0.20810 0.01635	Out-of- plane bending of molecule
624.03	0.31870	in- plane bending of molecule
518.34	7.07301	in- plane bending of C=O
510.09	52.51924	Out-of- plane bending of OH
469.60	16.19153	δ_s.of angle O=C-OH
359.29	0.00125	Out-of- plane bending of ring
349.43	2.77440	in- plane bending of C=O and in- plane bending of ring (vw.)
252.99	0.32866	υO-H and in- plane bending of ring (vw.)
125.88	0.37788	υO-H and in- plane bending of molecule
107.39	0.01725	Out-of- plane bending of molecule except ring bend.(vw)
21.55	0.41092	Out-of- plane bending of COOH and in- plane bending of ring (w)

υ_s.ar.C-H: symmetrical stretching vibration of aromatic C-H; ole.C-H bend. : Olefinic C-H bending;

Table (4): Ab initio calculated IR spectra data of cinamic acid.

Frequency,cm^{-1}	Intensity,$km.mol^{-1}$	Assignment
4254.57	6.00861	υO-H
3748.25	3.22387	υ_s. ar.C-H and υ C_8-H_{13}
3741.17	25.05317	$\upsilon_{as.}$ ar.C-H , υ C_8-H_{13},and vwυ C_7-H_{14}
3736.93 3731.18	6.99181 3.53203	$\upsilon_{as.}$ ar.C-H , υ C_8-H_{13},and wυ C_7-H_{14}
3723.76	0.96424	$\upsilon_{as.}$ ar.C-H and vwυ ole.C-H

3711.98	26.52874	υ C_7-H_{14}, wυ C_8-H_{13}, and vwυ$_{as.}$ ar.C-H
3709.68	14.82940	υ$_{as.}$ ar.C-H , υ C_7-H_{14},and wυ C_8-H_{13}
2108.67	152.72351	υ C=O
2014.35	20.46709	υC_7=C_8 and υC=O
1938.22 1911.03	0.07818 1.92113	υar. C=C
1790.46	17.46731	υar. C=C and υC_2-C_7
1727.06	19.37082	υar.C-C and υar. C=C
1651.07	64.23619	In-plane bend. of O-H
1563.84	0.79627	In-plane bend. of ar. C-H, C_7-H_{14}bend., and C_8-H_{14}bend(vw)
1533.55	4.80348	In-plane bend. of ole.C-H, vw ar. C-H bend. and vw.bend. of O-H
1486.12	39.84956	In-plane bend. of ole.C-H, υC_2-C_7, wυC- O and vw ar. C-H bend.
1430.16	110.92313	υC- O, υC_2-C_7,and υC_8-C_9
1406.48	58.46247	υC- O, υC_2-C_7, υC_8-C_9, in-plane bend. of both C-H, and ring
1377.77	1.16854	In-plane bend. of ar. C-H,and ole.C-H (vw)
1368.84	6.64637	In-plane bend. of ar. C-H,and ole.C-H (w),and vw υC- O
1270.72	0.20371	In-plane bend. of ring, wbend. of ole. C-H,and vw υC- O
1222.44	13.48255	out-of-plane bend. of ole. C-H
1210.76 1155.46	1.77766 1.33971	In-plane bend. of ring

1205.76	0.25406	out-of-plane bend. of ring and out-of-plane bend. of ole.C-H (vw)
1189.04	0.00000	out-of-plane bend. of ring
1173.70	2.15542	In-plane bend. of ring and vw υC- O
1120.73	0.03320	out-of-plane bend. of ring and out-of-plane bend. of ole.C-H (w)
1035.63 1027.73	3.25031 0.42721	out-of-plane bend. of both C_2-C_7H_{14}=C_8H_{13}-C_9=O and ring
1015.63	10.11487	υC- O,and υC_8-C_9
962.31	0.28111	In-plane bend. of ring, υC_2-C_7,and vw υC_8-C_9
901.83	20.86928	out-of-plane bend. of molecule except O-H
829.46	5.42715	out-of-plane bend. of (ring+ C_2-C_7) and w.bend. of C_8-C_9=O
727.27 543.04 308.15 92.39	11.95679 30.61627 0.26040 0.00190	out-of-plane bend. of molecule
714.23 711.78 545.63 371.36	1.53776 4.32518 6.22194 0.98675	in-plane bend. of molecule
606.69	47.12612	in-plane bend. of COOH and in-plane bend. of molecule (w)
570.56	61.20598	out-of -plane bend. of OH and out-of-plane bend. of molecule (w)
477.11	0.00364	out-of-plane bend. of ring
246.02	0.37110	υO-H and in- plane bending of molecule(w)

124.58	0.17988	out-of-plane bend. of $H_4C_7=C_8H_{13}-C_9(=O)-OH$
113.10	0.37821	υO-H and in- plane bending of molecule
31.68	0.22527	out-of-plane bend. of COOH and out-of-plane bend. of molecule

Table (5):PM_3 calculated IR spectra data of hippuric acid.

Frequency,cm^{-1}	Intensity,$km.mol^{-1}$	Assignment
3847.35	21.56523	υO-H
3347.29	11.24633	υN-H
3077.83	12.35265	$\upsilon_{s.}$ ar.C-H
3066.32 3057.24 3043.59 3018.79	21.38829 2.00306 10.33172 6.40082	$\upsilon_{as.}$ ar.C-H
2971.08	4.52248	$\upsilon_{s.}$C-H of CH_2
2895.64	3.58926	$\upsilon_{as.}$ C-H of CH_2
1973.68	152.17487	υ C=O of COOH
1895.58	141.16603	υ C=O of amide
1795.01	7.31951	υ_s C=C
1777.78	0.89401	υ_{as} C=C
1597.72	26.48782	υ_s C=C, υ C-C of ring, υ C_2-C_7, and υ C_7-N_9
1542.61	17.83261	υ_s C=C, υ C-C of ring, and υ C_7-N_9
1513.66	66.33114	In plane N-H bend., υ C-N,and υ C-C of ring

1442.69	71.84608	υ C_{11}-O_{13}
1385.51	71.41857	υ C_2-C_7, υ C_7-N_9, vw δ_s. CH_2, and in-plane bend. of ar. C-H (w)
1346.28	2.81326	δ_s.of CH_2, υ_s C=C and υ C- O (vw)
1328.01 1307.96	1.76030 0.11806	δ_s.of CH_2, υ_s C=C and υ C- O
1264.59	2.13320	ω CH_2, in plane O-H bend., in-plane bend. of ar. C-H,and in plane N-H bend.(vw)
1248.00	20.51093	In-plane bend. of ar. C-H, υ C_7-N_9,
1219.89	22.76963	in plane O-H bend., ω CH_2 (w)
1188.01	0.14793	In-plane bend. of ar. C-H, and in plane N-H bend.(vw)
1154.47	0.40020	In-plane bend. of ar. C-H
1121.27	0.22223	υ C_{10}-N_9 and in-plane bend. of ring
1112.37 1097.31	3.29870 2.89760	υ C_{10}-N_9 and in-plane bend. of ar. C-H
1052.73	0.63282	τ CH_2
1027.66	1.81749	In-plane bend. of ring
1022.15 949.13 603.07	0.07380 0.23699 0.39173	Out-of-plane bend. of Ph-CO
982.86	0.00887	Out-of-plane bend. of Ring
932.47	1.95043	υ C_{10}-C_{11} and υ C_{11}-O_{13}
897.47	0.65630	ρ CH_2 and out-of-plane bend. of CO of COOH
851.06	0.00921	Out-of-plane bend. of ar.

		C-H
844.93	2.79323	In-plane bend. of Ph-CO
791.09 693.62	5.35647 40.62939	Out-of-plane bend. of (CO , ar. C-H, and a part of ring)
647.98	5.60437	In-plane bend. of molecule except CH_2 and O-H
630.42	0.16835	In-plane bend. of ring
556.78 489.44	43.61280 22.83222	ρ CH_2 and out-of-plane bend. of COOH
526.33 -36.28	3.71353 2.89038	bending of molecule except ring
460.04	21.94062	δ_s.of angle O=C-OH
445.10	0.88877	δ_s.of angle O=C-OH and in-plane bend. of Ph-CO
416.18	0.33762	Out-of-plane bend. of Ph.(CO).N-H
354.04	0.11173	Out-of-plane bend. of ring
325.00 274.59	2.32811 2.84362	In-plane bend. of both C=O
232.28	0.73902	υO-H and in-plane bending of molecule except CH_2
198.31 107.24 10.73	2.01006 1.24193 0.63224	Out-of-plane bend. of molecule
88.32	0.12367	In-plane bend. of ring and υO-H
-27.07	0.11152	Out-of-plane bend. of COOH
-416.03	74.11139	Out-of-plane bend. of N-H

Table (6): Ab initio calculated IR spectra data of hippuric acid.

Frequency,cm^{-1}	Intensity,$km.mol^{-1}$	Assignment

4258.38	7.92722	υO-H
4183.10	54.03877	υN-H
3747.72	2.37683	$\upsilon_{s.}$ ar.C-H
3740.17 3732.83 3725.80 3711.83	11.34308 9.41858 1.56308 0.43506	$\upsilon_{as.}$ ar.C-H
3661.59	0.27681	$\upsilon_{as.}$ C-H of CH_2
3564.55	7.29636	$\upsilon_{s.}$C-H of CH_2
2135.16	89.54150	υ C=O of COOH
2055.35	92.70746	υ C=O of amide
1938.02	4.45705	υ_s C=C
1913.44	3.81245	$\upsilon_{as.}$ ar.C-H
1813.43	14.06750	$\delta_{s.}$of CH_2
1792.47	14.53522	$\upsilon_{as.}$ ar.C-H, υ C_3-C_7, υ C_7-N_9, in-plane bend. of N-H,and vw ω CH_2
1730.37 1717.89	250.80436 56.47721	In plane N-H bend., υ C_7-N_9 υ N_9- C_{10}, ω CH_2,and υ C-C, C=C of ring
1649.77	45.89661	In plane O-H bend.
1579.21	30.23470	ω CH_2, υ C_3-C_7, υ C_7-N_9, and in plane O-H bend.(w)
1549.70	0.69482	In-plane bend. of ar. C-H
1453.61	88.66297	υ C3-C7, in plane N-H bend., ω CH_2, and υ C_{11}-O_{13}
1422.96	2.37386	τ CH_2
1415.15	118.41261	υ C_{11}-O_{13} ,υ C3-C7, vw ω CH_2, and in plane N-H bend.(w)
1386.50	6.43671	υ C_{10}-N_9, υ C_3-C_7, and

		in-plane bend. of ar. C-H
1373.77	8.98951	υ C_{10}-N_9, in plane O-H bend.(w) , and in-plane bend. of ar. C-H
1361.36	8.75221	υ C_{10}-N_9, υ C_3-C_7, in plane O-H bend.(w) , and in-plane bend. of ar. C-H
1277.57	1.61919	In-plane bend. of ring
1242.96	21.04104	υ C-N and in-plane bend. of ring
1208.17 1191.28 1030.88 474.77	0.00005 0.02447 0.01825 0.10989	Out-of-plane bend. of ring
1204.54 1158.09 712.67	1.01436 1.93367 0.32708	In-plane bend. of ring
1167.38	3.57254	υ_s C=C
1162.47	0.00042	ρ CH_2 and out-of-plane bend. of C=O of COOH
1123.42 923.67 828.75 752.54 512.28	0.22080 1.87931 13.17199 22.49227 0.04713	Out-of-plane bend. of Ph-C=O
1011.92	27.35219	In-plane bend. of ring, in-plane bend. of angle C_7-N_9-C_{10}, and υ C_{11}-O_{13}
926.89	3.71947	skeletal vibrations
756.72	13.87780	In-plane bend. of molecule
616.65	77.49756	ρ CH_2 and out-of-plane bend. of COOH
599.40	41.37296	δ_s.of angle O=C-OH
584.82	14.62748 2.35957	bending of molecule except ring

530.69	34.59139	Out-of-plane bend. of COOH and w ρ CH_2
481.09	0.69749	bending of molecule except CH_2 and N-H
340.79 79.03	2.28476 0.13253	bending of molecule
270.49	2.35957	υ O-H and bending of molecule except ring
228.30	3.48321	υ O-H and bending of molecule
224.48	1.65046	Out-of-plane bend. of molecule except COOH
116.18 37.03 -25.44 -31.80	3.17741 0.81043 0.00273 1.61993	Out-of-plane bend. of molecule
-395.13	146.10451	Out-of-plane bend. of N-H

Table (7): IR Frequency,cm^{-1} and tentative assignments for adipic acid.

Frequency,cm^{-1}	Assignment
3124.68-2569.18	υO-H
1722.43-1676.14	υ C=O
1463.97	δ_s.CH_2
1427.32 1408.04 1357.89 1315.45	υ C- O , C-OH bending and υ_s COO
1290.38 1271.09 1201.65 1190.08	τ CH_2
1043.49	-
734.88	δ COO
690.52	ρ CH_2
514.99	-

Table (8): IR Frequency,cm^{-1} and tentative assignments for cinamic acid.

*

Frequency,cm^{-1}	Assignment
3059.1-2524.82	υO-H
1678.08 1627.92	υ C=O,COOH
1577.77	υ C=C
1492.9 145-.47	In-plane bending of C=C-H
1425.4	υ_s COO
1344.38 1315.45	υ C- O and OH bending*
1288.45 1228.66 1205.51 1176.58 1157.29	In-plane bending of ring CH bonds
985.62 972.12 933.55 871.82 765.74 705.96 677.01	Out-of-plane bending of both aromatic and alkene C-H
592.15 543.93 480.28	Ring deformation Out-of-plane ring bending

Both of these bands involve some interaction between C-O stretching and In-plane C-O-H bending.

Table (9): IR Frequency,cm^{-1} and tentative assignments for hippuric acid.

Frequency,cm^{-1}	Assignment
3344.57 3584.18 3072.6	υN-H
2939.52 2721.5 2692.63 2603.9	υ.C-H

2571.11 2478.5	
1759.08 1745.58	υ C=O,COOH
1622.13 1606.7 1600.92 1573.91 1564.27 1548.84	δN-H, δ H2O and υ C=C
1490.97 1446.61	C-H deformation of CH_2
1417.68 1396.46	υ_s COO
1334.74 1317.38 1303.88	δ.CH_2 and C-O-H bending
1257.59	υ C-C
1188.15 1174.65	δ.CH In-plane bending.
1080.14 1029.99 1001.06	ρ CH_2
943.19 879.54 848.68 806.25	υ C-C
723.31	δ COO
694.37 659.66 628.79 615.29 547.78 538.14 435.91	ring deformation

Discussion

The IR spectrum of adipic acid was calculated by PM3 (Table 1). It was found that no difference between symmetrical (3852.94 cm^{-1}, the two OH groups str in the same way) and asymmetrical (3852.87 cm^{-1}, O7-H12 group str opposite to stretching of O10-H11 group) stretching vibrations. This may be done to the low OH groups which located in two identical electronic and stero environments. Ab initio calculations of IR spectrum (Table 2) also showed a little difference between υ_s.O-H and υ_{as}.O-H but the intensity of the latter band in both PM3 and ab initio methods were much more (32.84261 and 19.70733 km.mol respectively than the intensity of υ_s.O-H bands (0.1573 and 0.00053 respectively too) [20]. The practical FT-IR of adipic acid showed one very strong band for OH stretching vibration in the range (3124.68-2569.18 cm^{-1}), also the other bands were almost strong and intense. Generally, the PM3 calculations of υOH was closer to practical υOH (after rescaled multiply by 0.95) than ab initio calculations of υOH [20]. The practical measurement of aliphatic C-H stretching bands are superimposed upon this strong extended (spreader) OH band. The sutiable structures at 2409.09, 2277.93, 2267.1, 2271.85 and 2121.70 cm^{-1} observed on the long wavelength side of the OH band which represents overtones and combination tone of fundamental bands occurring at longer wavelengths [23]. Ab initio asymmetrical stretching vibrations of aliphatic C-H bands in both adipic and hippuric acids υ_{as}.C-H were high frequencies than the corresponding asymmetrical stretching vibrations υ_s. The practical vibration (υ C-H of CH_2 group) of huppuric acid was at higher energies than those of adipic acid. This is completely expected because of the CH_2 group in huppuric acid is located under electron withdrawing effect which leads to make C-H bands stronger than those in adipic acid[24]. The PM3 calculations of υ_s ar.C-H in both cinamic and hippuric acids are the same frequency, while υ_{as} ar.C-H in cinamic acid is little frequency than in hippuric acid (Table 3 and 5). It was noted that PM3 calculationss of C7-H18 bond is stronger than C8-H13 bond due to the frequency of the first bond which calculated by PM3 method is higher than frequency of C8-H13 [20]. The frequency of symmetrical and asymmetrical stretching of aromatic C-H bonds was calculated by abinitio method in cinamic acid. The intensity of υ_s C=O is more Less than υ_{as} C=O but the difference of frequency is very little (υ_s is a little higher energy than υ_{as}) in both calculated spectra of adipic acid (Table 4). Abinitio calculations of υ C=O for hippuric acid give higher frequency than those in adipic and cinamic acids (Table 6) .This calculated sequence is completely consistent with practical spectra [13].The resonance in cinamic acid leads to decrease the stretching frequency of the carbonyl group while the resonance is completely absent in adipic acid. Indeed the electron withdrawing effect on carbonyl group of hippuric acid leads to strength this group and shows at high stretching frequency. The

stretching frequency of hippuric amide carbonyl group is less due to the conjugation of this group with phenyl group. It was released that PM3 method couldn't estimate the right stretching frequencies of the carbonyl groups for the three carboxylic acids. The practical FT-IR of adipic acid (Table 7) showed the υ C=O with in the frequency range of (1722.43-1676.14 cm^{-1}). It was also noted that the same manner for adipic acid (υ_s C-OH and υ_{as} C-OH) which were calculated by PM3 method, but these two stretching aren't apparent in an abinitio calculation of IR spectrum[18]. The frequency of υ_s C=C and υ_{as} C=C for both hippuric and cinamic acids (1795.71-1543.36 cm^{-1}) which was calculated by PM3 method. The same results are noted in abinitio spectra while abinito calculations υ_{as} C=C of hippuric acid is higher frequency than in cinamic acid due to the conjugation in the latter and this is consistent with practical FT-IR spectra [24]. Abinitio calculation of IR of adipic acid showed δ_sOH doped with ωCH_2 a twice all these bending modes which are higher energy than δ_s of angle O=C-OH which are also a similar with PM3 spectrum. In both spectra, the out of plane bending of OH is less energy than δ_s OH. There are two PM3 out of plane bending of COOH one of them is high energy than out of plane bending of OH and the other is less energy of the latter (negative wave number). Abinitio spectrum of adipic acid showed three out of plane bending of COOH: two of them are lesser energy the third one with negative wave number than out of plane bending of OH. While the PM3 calculations of IR of cinamic acid showed one out of plane bending of COOH doped with ring bending and both of abinitio bending of OH and COOH were doped also with ring bending[20]. Out of plane bending of OH in both IR abinitio and PM3 methods of hippuric acid isn't present and out of plane bending of COOH was also doped with ρ CH_2, whereas the abinitio spectrum showed additional negative wave number band for out of plane bending of N-H. Abinitio calculation of IR spectrum of adipic acid showed three bands out of plane bending of C=O and all of them were doped with τ CH_2 and ρ CH_2 modes. These bands were higher energy than of pure mode in of plane bending of C=O group. It seems that only the last band was present in PM3 spectra and abinitio spectrum showed in plane bending of all molecule lower energy followed by low intensity of energy band concerned with υ_{as}.O-H. The υ_{as}.O-H was doped with plane bending of all molecule and the other interesting band υ_s.O-H was also doped with plane bending of all molecule.

Furthermore, the PM3 spectrum showed only two bands of υ_{as}.O-H with low energy of skeletal vibrations without presence of υ_s.O-H in plane bending of molecule. This spectrum also showed one band plane bending of all molecule with other band out of plane bending of all molecule which is absent in abinitio spectrum. Generally, both PM3 and abinitio spectra cooperated each other to estimated IR bands of adipic acid. The PM3 and abinitio calculations of cinamic acid showed that υ

OH shifted to higher wave number compared with the two bands of υ OH in the aliphatic adipic acid and the reason may be the electron withdrawing effect of cinamic acid which is mentioned in practical spectra (Table 8). This table showed the opposite manner of υ OH band for adipic acid at higher wave number than that in cinamic acid therefore the both methods failed to estimate the right positions for υ OH band in both acids. With regard to the hippuric acid, the PM3 IR spectrum showed υ OH at lower energy than those of other acids but it was at higher energy in abinitio spectrum (Table 9). The reason seems the PM3 method has considered the –N-CH_2- group gives electrons density towards COOH group (the resonance is absent) but the reason of the difference in abinitio spectrum may result that OH group suffers more electron with drawing effect than those of other acids. It is seemed that theoretical results more reasonable and exactly agree with practical spectra[20] .

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