Material Science Research India Vol. **5**(1), 75-82 (2008)

Vibrational spectroscopic studies and DFT calculations of 4-hydroxyacetanilide

K. RAJU[1], G.GOPKUMAR[1], G. KRISHNAKUMAR[1], HEMA TRESA VARGHESE[2] and C. YOHANNAN PANICKER[3]*

[1]Department of Physics, University College, Trivandrum (India)
[2]Department of Physics, Fatima Mata National College, Kollam (India)
[3]Department of Physics, TKM College of Arts and Science, Kollam (India)

(Received: February 28, 2008; Accepted: May 20, 2008)

ABSTRACT

A complete vibrational spectrum analysis of 4-hydroxyacetanilide is performed. The wavenumbers are calculated on the basis of density functional theory using B3LYP/6-31G* basis set. Vibrational analysis indicates that the lowering of stretching wavenumbers of methyl group due to electronic effects simultaneously caused by inducation and hyperconjugation is due to the presence of the oxygen atom. Comparison of the observed fundamental vibrational wavenumbers of 4-hydroxyacetanilide with calculated results is found in agreement with the experimental data. The predicted infrared intensities and force constants are reported.

Key words: DFT, Infrared, Raman, hyperconjugation.

INTRODUCTION

Paracetamol (acetaminophen or N-acetyl-4-amino-phenol or 4-hydroxyl acetanilide) is a popular analgesic and antipyretic medication that is readily absorbed after administration and has few side effects and little toxicity when used in recommended dose[1-7]. After ingestion of an overdose quantity of paracetamol, the accumulation of toxic metabolites may cause severe and sometimes fatal hepatotoxicity and hephrotoxicity[8]. So, the accurate determination of paracetamol in pharmaceutical preparations and biological fluids has appeared especially attractive. For its measurement, many methods have been developed, such as fluorometry[9], chemiluminescence[10], electrochemical method[11], nuclear magnetic resonance, mass spectrometry[12], gas chromatography[13], and liquid chromatography[14-16]. Computational method is at present widely used for simulating IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. In the present study the IR, Raman and theoretical calculations of the wavenumbers of the title compound are reported.

Computational details

The vibrational wavenumbers were calculated using the Gaussian03 software package on a personal computer[17]. The density functional theoretical (DFT) computations were performed at the B3LYP/6-31G* level of theory to get the optimized geometry (Fig. 1) and vibrational wavenumbers of the normal modes of the title compound. The DFT partitions the electronic energy $E = E_T + E_V + E_J + E_{XC}$, where E_T, E_V and E_J are electronic kinetic energy, electron nuclear attraction and electron-electron repulsion terms, respectively. The electron correlation is taken into account in the DFT via the exchange-correlation term E_{XC}, which includes exchange energy arising from the anti-symmetry of quantum mechanical wavefunction and dynamic correlation in the motion of individual electron, and it makes DFT dominant over

conventional HF procedure[18]. DFT calculations were carried out with Becke's three-parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. All optimized structures (Table 1) were confirmed to be minimum energy conformations. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima in the potential surface. At the optimized structure of the examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface was found. The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The DFT hybrid B3LYP functional tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data[19]. Thus, a scaling factor of 0.9613 has been uniformly applied to the B3LYP calculated wavenumbers[18]. The observed disagreement between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry[20].

RESULTS AND DISCUSSION

The IR and Raman spectra of the title compound are downloaded from the website www.aist.go.jp. The calculated wavenumbers, observed IR and Raman bands together with their relative intensities and band assignments are given in Table 2.

Acetylamino group-NHC(=OMe) vibrations

The NH stretching vibration[21] in N-substituted acetamides appears strongly and broadly in the region 3280 ± 60 cm^{-1}. For the title compound, the strong band at 3326 cm^{-1} in the IR spectrum and the weak band at 3320 cm^{-1} in the Raman spectrum is assigned as νNH mode. The calculated value for this mode is 3437 cm^{-1}. The NH stretching wavenumber is red shifted by 111 cm^{-1}, in IR with a strong intensity from the computed wavenumber, which indicates the weakening of the N-H bond resulting in proton transfer to the neighbouring oxygen[22]. Methyl groups are generally referred to as electron-donating substituents in the aromatic ring system[23]. Absorption intensities in the infrared region provide much information of the nature of the chemical bonds and the effects due to intramolecular environment. Different theoretical models have been proposed for infrared intensities, which can reveal a picture of the charge distribution and charge mobility in the molecules. The wavenumbers of the vibrational modes of the methyl group are known to be influenced by a variety of interesting interactions such as electronic effects, inter-molecular hydrogen bonding and Fermi resonance[24]. Electronic effects such as back-donation and induction, mainly caused by the presence of oxygen atom adjacent to CH_3 group, can shift the position of CH stretching and bending modes[25,26]. The electronic effect, hyperconjugation, usually means the interaction of the oribitals of a methyl or methylene group with the π-orbitals of an adjacent C-C bond. When the hydrogen bonds become more acidic because of the release of electronic charge, the infrared C-H stretching intensity decreases and bending intensity increases[26]. In the spectra of methyl esters, the overlap of the regions in which both asymmetric stretchings[21] $\upsilon_{as}CH_3$ absorb with weak intensity (2990 ± 20 and 2965 ± 35 cm^{-1}) is not large. The computed wavenumbers of modes corresponding to the $\tilde{o}_{as}CH_3$ group are 3049 and 3014 cm^{-1}. In this mode two C-H bonds of the methyl group are extending while the third one is contracting. The symmetrical stretching mode υ_sCH_3 is expected in the range 2900 ± 45 cm^{-1} in which all the three C-H bonds extend and contract in phase[21]. The observed bands at 3036, 2930 cm^{-1} in the IR spectrum and 3030, 2934 cm^{-1} in the Raman spectrum are assigned to asymmetric and symmetric stretching modes of CH_3, respectively. This happens because of the hyperconjugation of the methyl group with the π-electrons in the aromatic ring, where the injection of negative electronic charge takes place from the CH_3 group to an adjacent portion of the molecule that contains the ð-electrons. In the title molecule, the methyl hydrogen bonds are subjected simultaneously to hyperconjugation and induction which cause the decrease in infrared intensities as reported in the literature for similar molecular systems[27].

Thus hyperconjugation and induction of the methyl group, causing changes in intensity in the infrared spectrum, clearly indicates that methyl hydrogens are directly involved in the donation of electronic charge. Two bending vibrations can occur within a methyl group. The first of these, the symmetrical bending vibration $\delta_s CH_3$ involves the in-phase bending of the C-H bonds. The second, the asymmetric bending mode $\delta_{as} CH_3$ involves out-of-phase bending of the C-H bonds[28]. The methyl asymmetric deformations[21] provide a weak to moderate band in the regions 1450 ± 30 cm^{-1} and 1420 ± 20 cm^{-1}. As contrasted with the very weak stretchings, the methyl symmetric deformation[21] appears more strongly in the region 1365 ± 10 cm^{-1}. The DFT calculations give 1458, 1444 and 1370 cm^{-1} as $\delta_{as} CH_3$ and $\delta_s CH_3$ respectively, for the title compound. Experimentally the asymmetric bending vibrations are not observed while strong symmetric bending vibration is observed at 1373 cm^{-1} in both spectra. El-Shahawy *et al*.[29] reported 1440 and 1370 cm^{-1} as $\delta_{as} CH_3$ and $\delta_s CH_3$ modes. The enhancement in intensity of the bending mode is due to the presence of C=O adjacent to CH_3 group[30] which is in good agreement with the calculated values. The relatively large value of IR intensity of the symmetrical bending mode suggests a large positive charge localized on the hydrogen, which further supports the occurrence of hyperconjugation. Hydrogen bonding originates from an attractive interaction between the electron-deficient hydrogen donor group (A-H) and a region of high electron density acceptor atom (B), leading to a variation of H…B distance than the Van-der Walls radii of the isolated H and B atoms. Although the interaction energy of a C-H…O hydrogen bond is less than those of typical N-H…O and O-H…O bonds, the C-H type hydrogen bond plays an important role in determining higher-order structure in proteins, molecular structure and conformation and crystal packing. The complexes involving this shift are often accompanied by a significant decrease in its infrared intensity[31-33]. In the C-H…O hydrogen bond, a charge transfer from the lone pairs of the electron donor is directed mainly to the antibonding orbitals in the remote part of the complex, thereby causing elongation in that part of the complex. This primary effect of elongation is accompanied by a secondary effect of structural reorganization of the proton donor, leading to contraction of the C-H bond. Therefore, a C-H…O hydrogen bond is considered as an 'improper hydrogen bond' or a 'blue shifting H-bond'. Blue shifting, hydrogen bonds are characterized by a contraction or strengthening of the C-H bond, a blue shift of the C-H stretching vibrational mode and a reduction of its infrared intensity, features that are in sharp contrast to those associated with the conventional hydrogen bonds. The aromatic C-H stretching modes appear at 3165 and 3114 cm^{-1} in the IR spectrum as weak bands. The corresponding stretching modes are computed at 3096 and 3094 cm^{-1}, which explains that the observed vibrational wavenumbers are larger by 69 and 20 cm^{-1} than the computed values from their normal coordinates. The bond lengths of C_5-H_{11}, C_6-H_{12}, C_3-H_9, C_2-H_8 are calculated to be 1.0869, 1.0853, 1.0849, 1.0885 Å, respectively, from the optimized geometry. The C-H bond length corresponding to C_3-H_9, C_6-H_{12}, are shortened compared to other CH bond lengths, confirming the existence of the blue shifting hydrogen bond. The carbonyl stretching C=O vibration (Amide I)[21,22] is expected in the region 1715 -1680 cm^{-1} and in the present study this mode appears at 1667 cm^{-1} in the IR spectrum and at 1651 cm^{-1} in the Raman spectrum as intense bands. The DFT calculations give this mode at 1722 cm^{-1}. El.Shahawy *et al*[29] reported a value of 1640 cm^{-1} in the IR spectrum as υC=O for paracetamol. The deviation of the calculated wavenumber for this mode can be attributed to the under estimation of the large degree of ð-electron delocalization due to conjugation of the molecule[34]. The intensity of carbonyl group can increase because of conjugation or formation of hydrogen bonds. The increase of conjugation, therefore, leads to the intensification of the Raman lines as well as the increased infrared band intensities. The conjugation and influence of intermolecular hydrogen-bonding results in the lowering of the stretching wavenumbers. The bands associated with the C=O stretching mode are found to be strongly and simultaneously active in both IR and Raman spectra. This phenomenon is quite unusual, since, generally, even in the absence of inversion symmetry, the infrared and Raman spectra are complementary; in most cases, the strongest bands in the Raman spectrum are weak in the IR spectrum and vice versa. However, the ICT from the donor to acceptor group through a single-double bond conjugated path can induce large variations

of both the molecular dipole moment and molecular polarizability, making the IR and Raman activities strong at the same time. Thus in the title compound, simultaneous IR and Raman activation of C=O stretching mode clearly explains a charge-transfer interaction between donor and acceptor through the ð-conjugated path[35,36]. The CNH vibration in which N and H atoms move in opposite direction of carbon atom in the amide moiety appears at 1509 cm^{-1} in both spectra and at 1506 cm^{-1} theoretically and the CNH vibration in which N and H atoms move in the same direction of carbon atom in the amide group appear at 1250 cm^{-1} in Raman and 1258 cm^{-1} (DFT)[29,37,38]. The NH rock in the plane is observed at 1173 (IR), 1170 (Raman) and 1161 cm^{-1} theoretically[29]. The out-of-plane wagging[21] of NH is moderately active with a broad band in the region 790 ± 70 cm^{-1} and the band at 716 cm^{-1} (IR), 720 cm^{-1} in Raman and 754 cm^{-1} (DFT) is assigned as this mode. El-Shahawy *et al*.[29] reported a value 720 cm^{-1} for this mode. The C-N stretching vibration (Amide III)[21] coupled with the δNH, is moderately to strongly active in the region 1275 ± 55 cm^{-1}. El-Shahawy *et al*.[29] observed a band at 1320 cm^{-1} in the IR spectrum as this υC-N mode. In the present case, the band at 1329 cm^{-1} (IR), 1326 (Raman) and 1327 cm^{-1} (DFT) is assigned as the υC-N mode. The methyl rocks[21] are observed as weak to medium bands in the region 1090 ± 40 and 1015 ± 35 cm^{-1}. The bands calculated at 1090 and 1026 cm^{-1} are assigned as ρCH_3 modes. The bands observed at 1108, 1020 cm in the IR spectrum and the two weak bands at 1100 and 1020 cm^{-1} in the Raman spectrum are assigned as rocking modes of the methyl group.. The υC-C[21] absorbs weakly to moderately in the region 915 ± 65 cm^{-1}. N-Phenyl-substituted acetamides[21] give this C-C stretching vibration near 965 cm^{-1}. For the title compound the band at 970 (IR), 971 (Raman) and 992 cm^{-1} (DFT) is assigned as νC-C mode.The δC=O in-plane deformation (amide IV)[21] has been found in the region 625 ± 70 cm^{-1} and the band at 605 cm^{-1} (IR), 618 cm^{-1} (DFT) is assigned as this mode. The C=O out-of-plane deformation (Amide VI)[21] is in the range 540 ± 80 cm^{-1} and the DFT calculation give this mode at 493 cm^{-1}. Correspondingly a band is observed at 504 cm^{-1} in the IR spectrum. Acetylamino compounds[21] display the in-plane skeletal N-C-C deformation in the region 420 ± 55 cm^{-1} and the external –N-C deformation in the region 310 ± 65 cm^{-1}. The NHC(=O)Me torsion[21] is expected in the region 225 ± 65 cm^{-1}. Usually the methyl torsion absorbs at 200 ± 65 cm^{-1} and the C(=O)Me torsion at lower wavenumbers, 100 ± 40 cm^{-1} [21]. For the title compound, these skeletal deformations and torsions are found below 400 cm^{-1}.

Hydroxyl group vibrations

The OH group provides three normal vibrations υOH, δOH and γOH, of which not only the stretching vibration but also the out-of-plane deformations are good group vibrations. The DFT calculations give the õOH band at 3607 cm^{-1}. The in-plane OH deformation[21] is expected in the region 1400 ± 40 cm^{-1} and the band at 1394 cm^{-1} is assigned as this mode. The stretching of the hydroxyl group with respect to the phenyl moiety $\upsilon(C\text{-}O)_h$ appears at 1228 cm^{-1} in the IR spectrum, 1239 cm^{-1} in the Raman spectrum and at 1209 cm^{-1} theoretically. This band is expected in the region 1220± 40 cm^{-1} [37,39]. The out-of-plane OH deformation is observed at 626 cm^{-1} in the IR spectrum 630 cm^{-1} in the Raman spectrum and at 633 cm^{-1} theoretically, which is expected in the region 650 ± 80 cm^{-1} [21]. For paracetamol, $\upsilon(C\text{-}O)_h$ and γOH are reported at 1240 and 620 cm^{-1} respectively[29].

Phenyl ring vibrations

The aromatic CH stretching vibrations[21] absorb weakly to moderately between 3120 and 3000 cm^{-1}. The DFT calculations give bands at 3096, 3094, 3071 and 3050 cm^{-1}. Experimentally, we have observed bands at 3165, 3114 cm^{-1} in the IR spectrum and at 3105, 3065 cm^{-1} in the Raman spectrum. The benzene ring possess 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[21]. With heavy substitutents, the bands tend to shift to somewhat lower wavenumbers and the greater the number of substituents on the ring, the broader the absorptions regions[21]. In the case of C=O substitution, the band near 1490 cm^{-1} can be very weak[21]. The fifth ring stretching vibration which active near 1315 ± 65 cm^{-1}, a region that overlaps strongly with that of the CH in-plane deformation[21]. 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

other wise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from the other modes. For the title compound, the õPh modes are observed at 1611, 1587, 1509, 1444 cm^{-1} in the IR spectrum and at 1612, 1564, 1509, 1448 cm^{-1} in the Raman spectrum. The DFT calculation showed this modes at 1614, 1585, 1506, 1451 and 1302 cm^{-1}. The mode at 1506 cm^{-1} is not pure but contains a contribution from δNH mode. According to Roeges[21] υPh modes are expected in the region 1615 - 1280 cm^{-1}. The sixth ring stretching vibration or ring breathing mode[21,37] is expected in the region 790 ± 70 cm^{-1}. For the title compound the ring breathing mode appears at 800 cm^{-1} in the Raman spectrum, 809 cm^{-1} in the IR spectrum and at 812 cm^{-1} theoretically. For para substituted benzenes, the δCH modes[21] are seen in the range 995 – 1315 cm^{-1}. Bands observed at 1261, 1108 cm^{-1} in the IR spectrum and at 1260 cm^{-1} in the Raman spectrum are

Table 1: Optimized geometrical parameters of 4-Hydroxyacetanilide, atom labeling is according to Fig. 1.

Bond lengths (Å)							
C_1–C_2	1.3977	C_1–C_6	1.3996	C_1–O_7	1.3674	C_2–C_3	1.3947
C_2–H_8	1.0885	C_3–C_4	1.3992	C_3–H_9	1.0849	C_4–C_5	1.4036
C_4–N_{10}	1.4195	C_5–C_6	1.3899	C_5–H_{11}	1.0869	C_6–H_{12}	1.0853
O_7–H_{13}	0.9698	H_9–H_{19}	2.4698	N_{10}–C_{14}	1.3831	N_{10}–H_{15}	1.0140
C_{14}–O_{16}	1.2230	C_{14}–C_{17}	1.5189	C_{17}–H_{18}	1.0915	C_{17}–H_{19}	1.0962
C_{17}–H_{20}	1.0930						
Bond angles (°)							
A(2,1,6)	119.9	A(2,1,7)	123.0	A(6,1,7)	117.4	A(1,2,3)	120.2
A(1,2,8)	120.1	A(3,2,8)	119.7	A(2,3,4)	120.6	A(2,3,9)	119.6
A(4,3,9)	119.8	A(3,4,5)	118.6	A(3,4,10)	122.0	A(5,4,10)	119.4
A(4,5,6)	121.0	A(4,5,11)	119.2	A(6,5,11)	119.7	A(1,6,5)	119.9
A(1,6,12	119.0	A(5,6,12)	121.1	A(1,7,13)	109.1	A(3,9,19)	119.5
A(4,10,14)	130.6	A(4,10,15)	117.2	A(14,10,15)	111.8	A(10,14,16)	119.8
A(10,14,17)	118.1	A(16,14,17)	122.0	A(14,17,18)	107.4	A(14,17,19)	110.2
A(14,17,20)	113.1	A(18,17,19)	107.8	A(18,17,20)	110.1	A(19,17,20)	108.0
A(9,19,17)	99.5						
Dihedtral angles (°)							
D(6,1,2,3)	0.5	D(6,1,2,8)	179.0	D(7,1,2,3)	-179.3		
D(7,1,2,8)	-0.7	D(2,1,6,5)	1.0	D(2,1,6,12)	-179.8		
D(7,1,6,5)	-179.2	D(7,1,6,12)	-0.1	D(2,1,7,13)	0.0		
D(6,1,7,13)	-179.7	D(1,2,3,4)	-1.9	D(1,2,3,9)	177.2		
D(8,2,3,4)	179.6	D(8,2,3,9)	-1.4	D(2,3,4,5)	1.8		
D(2,3,4,10)	179.2	D(9,3,4,5)	-177.3	D(9,3,4,10)	0.2		
D(2,3,9,19)	133.1	D(4,3,9,19)	-47.9	D(3,4,5,6)	-0.3		
D(3,4,5,11)	-180.0	D(10,4,5,6)	-177.8	D(10,4,5,11)	2.5		
D(3,4,10,14)	52.7	D(3,4,10,15)	-134.3	D(5,4,10,14)	-129.9		
D(5,4,10,15)	43.1	D(4,5,6,1)	-1.1	D(4,5,6,12)	179.8		
D(11,5,6,1)	178.6	D(11,5,6,12)	-0.6	D(3,9,19,17)	11.4		
D(4,10,14,16)	178.9	D(4,10,14,17)	-0.9	D(15,10,14,16)	5.6		
D(15,10,14,17)	-174.2	D(10,14,17,18)	154.2	D(10,14,17,19)	-88.6		
D(10,14,17,20)	32.5	D(16,14,17,18)	-25.6	D(16,14,17,19)	91.6		
D(16,14,17,20)	-147.4	D(14,17,19,9)	67.9	D(18,17,19,9)	-175.2		
D(20,17,19,9)	-56.2						

Table 2: Calculated wavenumbers, IR and Raman bands positions (cm^{-1}) and assignments

υ_{cal}	υ_{IR}	υ_{Raman}	IR intensities (KM/Mole)	Force constants (mDyne/A)	Assignments
3607	-	-	49.33	8.8419	υOH
3437	3326 s	3320 w	22.63	8.0961	υNH
3096	3165 sbr	3105 w	1.89	6.6847	υCH
3094	-	-	11.89	6.6660	υCH
3071	3114 w	3065 m	8.23	6.5495	υCH
3050	-	-	13.57	6.4703	υCH
3049	3036 w	3030 w	18.11	6.5365	$\upsilon_{as}CH_3$
3014	-	-	8.83	6.3490	$\upsilon_{as}CH_3$
2949	2930 w	2934 m	3.54	5.7633	$\upsilon_{s}CH_3$
1722	1667 vvs	1651 vs	452.70	15.0396	υC=O
1614	1611 s	1612 vs	8.61	10.0609	υPh
1585	1587 vs	1564 s	8.48	9.5273	υPh
1506	1509 vs	1509 w	212.94	4.0611	δNH, υPh
1458	-	-	21.86	1.6649	$\delta_{as}CH_3$
1451	1444 s	1448 m	30.63	2.4228	υPh
1444	-	-	24.78	1.4288	$\delta_{as}CH_3$
1394	-	-	6.71	2.5476	δOH
1370	1373 m	1373 s	79.84	1.6812	$\delta_{s}CH_3$
1327	1329 m	1326 vvs	16.53	2.5607	υC-N
1302	-		223.01	2.6256	υPh
1290	1261 vs	1260 s	10.29	2.5946	δCH
1258	-	1250 m	178.60	3.3017	δNH
1209	1228 s	1239 vs	44.69	2.1457	$\upsilon(C\text{-}O)_h$
1161	1173 m	1170 vs	139.37	1.1769	ρNH
1155	-	-	42.89	0.9801	δCH
1090	1108 m	1100 w	15.47	1.0142	ρCH_3 , δCH
1026	1020 w	1020 w	7.66	1.1472	δCH, ρCH_3
996	-	-	27.72	1.0051	δCH
992	970 w	971 w	1.36	1.5654	υC-C methyl
916	-	-	0.17	0.7133	γCH
896	-	-	2.50	0.7701	γCH
892	839 s	851 vs	3.10	1.4153	γCH
815	-	837 m	28.57	0.7618	γCH
812	809 s	800 s	14.00	1.8293	Ring breathing
781	797 m	-	10.85	0.5150	δPh(X)
754	716 m	720 m	5.24	1.4537	(γ)ωNH
688	689 w	664 s	2.43	1.2831	γPh
633	626 w	630 w	7.00	1.4822	γOH
618	605 w	-	72.20	0.4675	δC=O
578	-	-	14.12	1.1099	γPh
522	521 m	507 m	20.21	0.4653	γPh(X)
493	504 m	-	43.73	0.2505	γC=O
485	-	468 m	6.22	0.3891	δPh(X)
419	-	-	3.38	0.4449	γPh
410	-	394 s	1.11	0.3500	δN-C-C

Table 2 cont.

358	-	-	1.41	0.4540	δCO(X)
347	-	-	6.57	0.5631	δCN(X)
339	-	332 m	118.07	0.0805	δN-C
310	-	-	6.41	0.2913	τNHC(=O)Me
193	-	217 s	1.10	0.1136	τCH_3
142	-	154 m	0.05	0.0133	γCO(X)
98	-	-	1.32	0.0320	γCN(X)
59	-	-	1.31	0.0183	τC(=O)Me
37	-	-	2.33	0.0030	τPh

υ, stretching; δ, in-plane deformation; γ, out-of-plane deformation; ω, wagging; ρ, rocking; τ, torsional; s, strong; m, medium; w, weak; v, very; br, broad; Ph, phenyl; X, substituent sensitive; Me, methyl; Subscript: as, asymmetric; s, symmetric; h, hydroxyl;

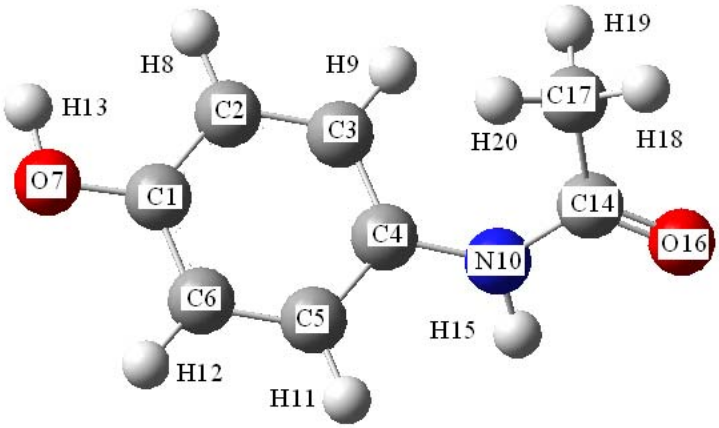

Fig. 1. Optimized geometry of 4-hydroxy acetanilide

assigned as δCH modes. The DFT calculations give these δCH modes at 1290, 1155, 1090 and 996 cm^{-1}. Some of the δCH bands are not pure but contain a significant contribution from methyl rocking modes. The C-H out-of-plane deformations[21] are observed between 1000 and 700 cm^{-1}. Generally the C-H out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. These γCH modes are observed at 839 cm^{-1} in the IR spectrum and at 851, 837 cm^{-1} in the Raman spectrum. The DFT calculations give these modes at 916, 896, 892 and 815 cm^{-1}. The strong CH out-of-plane deformation band occurring at 840 ± 50 cm^{-1} is typical for 1,4-disubstituted benzenes[21]. For the title compound a strong band is observed at 839 cm^{-1} in the IR spectrum and at 851 cm^{-1} in the Raman spectrum. Again according to literature[21,38] a lower γCH absorbs in the neighbourhood 820 ± 45 cm^{-1}, but is much weaker or infrared inactive. The ring planar deformation modes are observed at 689, 521 cm^{-1} in the IR spectrum and at 664, 507 , 468 cm^{-1} in the Raman spectrum. The DFT calculations give these modes at 781, 688, 578, 522, 485, 419 cm^{-1}.

All the carbon-carbon bond lengths in the benzene ring, lie in the range 1.3947-1.4036 Å and C-H bond lengths in the range 1.0849-1.0885 Å. Here for the title compound, benzene is a regular hexagon with bond lengths somewhere in between the normal values for a single (1.54 Å) and a double (1.33 Å) bond[40]. The carbon-oxygen (phenolate) C1-O7 distance 1.3674 Å is in agreement with the average distance of 1.362 Å found among phenols[41].

REFERENCES

1. MacConnachieA.M., *Intensive Crit. Care Nurs*.**13**: 238 (1997).
2. Dic.E, Ozdemi.Ar, Baleanu.D, *Talanta*, **65**: 36 (2005)**.**
3. BIvanova.B, *J. Mol. Struct*. **738**: 233 (2005).
4. Jan Mens.M.A., *Best Pract. Res. Chin. Rheumat*. **19**: 609 (2005).
5. Xu.C, Li,B. *Spectrochim. Acta* **60[a]**: 1861 (2004).
6. Moreira.A.B., OliveiraH.B.M., Atvars.T.D.Z., DiasI.L.T., NetoG.O., ZagattoE.A.G., Kubota.L.T., *Anal. Chim. Acta* **539**: 257 (2005).
7. BinevL.G., Vassileva-Boyadjieva; Binev.Y.I., *J. Mol. Struct*. **447**: 235 (1998).
8. Moffat, A.C., *Clarks Isolation and Identification of Drugs*, second ed., The Pharmaceutical Press, London. (1986).
9. Vilchez.J.L., Blanc.R, Avidad.R, Navalon.A, *J. Pharm. Biomed*. **13**: 119 (1995).
10. Easwaramoorth.D., Yu.Y, Huang.H, *Anal. Chim. Acta* **439**: 95 (2001).
11. Tanaka.H, Dasgupta.P.K., Huang.J, *J. Anal. Chem*. **72**: 4713 (2000).
12. Shockcor.J.P., Linger.S.E., Wilson.L.D., Foxall.P.J.D., Nicholson.J.K., Lindon.J.C., *Anal. Chem*. **68**: 4431 (1996).
13. Murray.S, Boobis, A.R, *J. Chromatogr*. **33**: 355 (1991).
14. GoicoecheaA.G., L.de Alda.M.J., Vila Jato. J.L., *J. Liq. Chromatogr*. **18**: 3257 (1995).
15. Heitmeier.S., Blaschke.G, *J. Chromatogr*. *B* **721**: 93 (1991).
16. Alshari, J.T., Tsan-Zon.M.L., *Anal. Chim. Acta* **443**: 165 (2001).
17. Frisch.M.J., et al. Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, (2004).
18. Foresman, J.B., Frisch.E., *Exploring Chemistry with Electronic Structure Methods; a Guide to Using Gaussian*, Gaussian Inc., Pittsburg, PA (1996).
19. Scott, A.P., Radom.L, *J. Phys. Chem*. **100**: 16503 (1996).
20. Rauhut, G, Pauly.P, *J. Phys*. **99**: 3093 (1995).
21. Roeges, N.P.G., *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures,* Wiley, New York (1994).
22. Barthes.M, De Nunzio.G, G.Ribet, *Synth. Met*. **76**: 337 (1996).
23. Tzeng.W.B., Narayana.K, Lin.J.L., Tung.C.C, *Spectrochim. Acta* **55A**: 153 (1999).
24. Kurtz.S.K., Perry.T.T., *J. Appl. Phys*. **39**: 3798 (1968).
25. Smith.B., *Infrared Spectral Interpretation, a Systematic Approach*, CRC Press, Washington DC. (1999).
26. Gussoni.M., Castiglioni.C.D., *J. Mol. Struct*., **5121**: 1 (2000)**.**
27. Gussoni.M., Castiglioni.C., Ramos.H.N., Rui.M.C., Zerbi.G., *J. Mol. Struct*. **224**: 445 (1990).
28. Silverstein.R.M., WebsterF.X., *Spectrometric Identification of Organic Compounds*, sixth ed. Wiley, Asia (2003).
29. El-ShahawyA.S.,Ahmed.S.M., Sayed.N.K., *Spectrochim. Acta* **66A**: 143 (2007).
30. Lin-Vien.D., Colthup.N.B., Fatley.W.G., Graselli.J.G., *The Hand Book of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, London (1991).
31. Sundararajan, K., Sankaran, K., Viswanathan, K.S., *J.Mol. Struct*., **733**: 187 (2005).
32. Montejo.M., Navarro.A., Kealey.G.J., Vazquez.J., Lopez Gonzalez J.J., *J. Am. Chem. Soc*., **126**(46): 15087 (2004).
33. Flakus.H.T., Chelmecki.M., *Spectrochim. Acta* **58**A: 179 (2002).
34. Panicker.C.Y., Varghese.H.T., Philip.D., Nogueira.H.I.S., Castkova, K.; *Spectrochim. Acta* Part A doi:10:1016/j.saa.2006.09.042.
35. Ruiz Delgado.M.C., Hernandez.V., Casado.J., Lopez Navarrete.J.T., Raimundo.J.M., Blanhard.P., Ronacli. J., *J. Mol. Struct*., **151**: 651 (2003).
36. Del Zoppo.M., Castiglioni.C., Zuhani.P., Zerbi.G., *Synth. Met*., **85**: 1043 (1997).
37. Varsanyi.G., *Assignments of Vibrational Spectra of Seven Hundred Benzene derivatives*, Wiley, New York (1974).
38. Colthup.N.B., Daly.L.H., Wiberly.S.E., *Introduction to Infrared and Raman Spectroscopy*, 2nd ed. Academic Press, New York (1975).
39. Varsanyi, G., Sohar.P., *Acta Chim. Acad. Sci. Hung*. **76**: 243 (1973).
40. Sykes.P., *A Guide Book to Mechanism in Organic Chemistry*, 6th ed. Pearson Education, India (2004).
41. Allen.F.H., Kennard.O., Watson.D.G., Brammer.L., Orpen.A.G., Taylor.R., *J. Chem. Soc, Perkin Trans*. **2**: S! –S19 (1987)**.**