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IR spectral and structural changes caused by the conversion of acetanilide into azanion

E .A. Velcheva*, Z. I. Glavcheva, B.A. Stamboliyska

Department of Structural Organic Analysis, Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 9, 1113 Sofia, Bulgaria

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The structures of acetanilide azanion and of its ^{15}N labelled analogue have been studied by means of both IR spectra and DFT calculation, employing the B3LYP functional and 6-311+G(2df,p) basis set. A good agreement has been found between the theoretical and experimental vibrational characteristic of the particles studied. The conversion of acetanilide molecule into the azanion causes 150 cm^{-1} decrease in the carbonyl stretching frequency, threefold increase in the integrated intensity of the corresponding IR band and other essential spectral changes. According to the calculations, the structural changes in the steric structure caused by this conversion take place *at* and *next to* the azanionic center. The new (azanionic) charge is distributed as follows: -0.304 e^- and -0.346 e^- are delocalized over the phenyl and acetyl groups and -0.349 e^- of its remained localized at the azanionic centre.

Keywords: N-phenylacetamide, anion, DFT

INTRODUCTION

The structure of organic anions is of general interest, as in living organisms part of bioactive molecules are dissociated in the body liquids, so that certain physiological actions are assumed to be due to its solvated anions. However, the highly reactive nature of anionic species has limited their structural characterization. The conversions of neutral molecule into radical-anions, carbanions, azanion, *etc*. are accompanied by essential changes in the vibration spectra. So, these changes are very informative for the structural variations caused by the same convertions [1]. The structure of large series of organic molecules and their anions have been successfully studied recently on the basis of experimental IR spectra combined with DFT computations [2-6]. The title compound is an interesting and convenient object of the molecule → anion conversions investigations, as it contains the (-CO-NH-) characteristic group and can be easily converted into a stable azanion.

Acetanilide, (N-phenylacetamide) was the first analgesic and antipyretic synthetic drug and was introduced into medical practice under the name of Antifebrin by Cahn and Hepp in 1886 [7]. The discovery of acetanilide as effective therapeutic agent was leading to the development of many new drugs, structural analogues, with similar or different pharmacological properties [8]. In the body acetanilide is mostly converted to p-hydroxyacetanilide [9], which has replaced acetanilide in therapy because it is less likely to induce blood disorders.

The early work on infrared (IR) spectra of acetanilide was reviewed by Crooks [10], Mann and Thompson [11], Abbott *et al.* [12]. A detailed empirical assignment of IR and Raman bands of acetanilide was reported about 50 years ago [13]. The complete IR band assignment of the acetanilide molecule was recently performed using ab initio Hartree–Fock (HF) [9] and DFT calculations [14,15]. The carbonyl C=O stretching frequencies and intensities of IR bands in series of substituted acetanilides were found to correlate with both Hammett's substituent constants and certain indices computed within ab initio and DFT methods [16-18]. IR spectra of a series of various carboxamide azanions were studied by Ognyanova and coworkers [19]. The authors reported that the stretching vibration frequencies of the amide C=O shifts downward depending on the substituents. Neither the detailed IR spectra nor structure of acetanilide azanion have been studied theoretically or experimentally. The purpose of the present investigation is to follow the spectral and structural changes, caused by the conversion of acetanilide molecule into the corresponding azanion on the basis of both DFT computations and spectroscopic experiments.

EXPERIMENTAL AND COMPUTATIONS

Acetanilide (Aldrich, 99%) was used without additional purification. We prepared acetanilide-^{15}N from aniline-^{15}N (VEB-Berlin-Chemie, 97.2% at. Enrichment) and acetic anhydride. The

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* To whom all correspondence should be sent:
E-mail: ev@orgchm.bas.bg

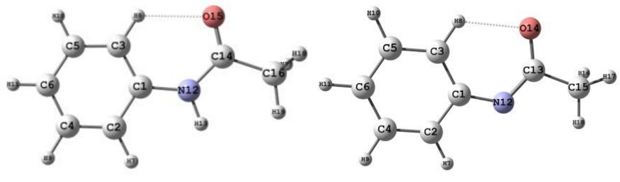
corresponding acetanilide azanion (counter ion Na$^+$) and its isotope-labeled derivative were prepared by adding dimethyl sulfoxide (DMSO/DMSO-d_6) solutions of acetanilide and acetanilide -^{15}N to excess of dry sodium methoxide –d_0 and –d_3, and filtration of the reaction mixture by a syringe filter. The conversion of the parent isotopomeric compounds into azanions under these conditions (solvent, concentrations, counter ion) is practically complete: no bands of the parent compounds can be seen in the spectra after metalation. IR spectra were measured on Bruker Tensor 27 Fourier transform infrared (FTIR) spectrophotometer in a CaF$_2$ cell of 0.13 mm (0.10 – 0.15 mol l^{-1} DMSO/DMSO-d_6 solutions), at a resolution of 1 cm^{-1} and 64 scans.

The quantum chemical calculations were performed using the Gaussian 09 package [20]. The geometry optimizations of the structures investigated were done without symmetry restrictions, using density functional theory (DFT). We employed B3LYP hybrid functional, which combines Becke's three-parameter nonlocal exchange with the correlation functional of Lee and coworkers [21,22], adopting 6-311+G(2df,p) basis sets. The stationary points found on the molecular potential energy hypersurfaces were characterized using standard harmonic vibrational analysis. The theoretical vibrational spectra were interpreted by means of potential energy distributions (PEDs) using VEDA 4 program [23]. For a better correspondence between experimental and calculated values, we modified the results using the empirical scaling factors [24].

RESULTS AND DISCUSSIONS

Energy analysis

All conformers of acetanilides and its deprotonated form have determined from rotation about Ph-N and N-C bonds. The structures of the most stable conformers are shown in Scheme 1.



A **B**

Scheme 1. B3LYP/6311+G(2df,p) optimized structures of the most stable conformers of acetanilide molecule A and its azanion B.

Both structures of molecule and azanion correspond to *trans*-type conformers (with respect to the phenyl and methyl groups). According to the B3LYP/6-311+G(2df,p) calculations the *cis* conformers of molecule are less stable than the *trans* form by 11.6 kJmol^{-1}. This result is with agreement with the theoretical study of Ilieva *at al.*[17]. The presence of the same conformer was also established by crystallographic analysis[25,26] and experimental and IR spectral data in solution [16]. According to the theoretical data, the *trans* conformer of the azanion is the more stable by the 21.6 kJmol^{-1}.

The calculated total energies of the studied species are as follow:

E_{tot}= -440.299988561 H for the acetanilide

E_{tot}= -439.7337264 H for the acetanilide azanion

The energy difference ED = E (anion) – E (molecule) can be used as an approximate measure of pKa of a given compound in the gas phase [27]. Georgieva and Velcheva [28] have found that ED values of series of C-H, N-H and O-H acids correlate fairly well (correlation coefficient R = 0.94) with the corresponding pKa values, measured in DMSO. Having in mind ED = 1489.06 H and the correlation equation:

$$\text{pKa (DMSO)} = 0.11507\text{ED} - 150.04 \text{ kJ mol}^{-1}$$

we estimated a ‘‘theoretical’’ pKa value of acetanilide at 21.0 in excellent agreement with the experimental value of 21.5 in DMSO [29] .

Infrared spectra

Organic anions are not soluble in common spectroscopic solvents and usually react with them. So, polar aprotic solvents, most frequently DMSO, are used to study the IR spectra of organic anionic derivatives [2-6,30].

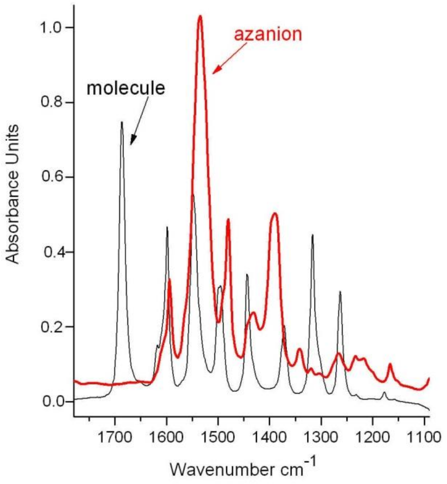


Fig. 1. IR spectra (0.12 mol l^{-1} in DMSO-d_6) of acetanilide molecule and its azanion.

Acetanilide azanion (e.g., acetanilide itself) is highly soluble and very stable in DMSO. To perform a correct comparison of the IR spectra of acetanilide isotopomers with those of their azanions, we shall consider their DMSO solution spectra. As in the preceding subsection, we shall now use theoretical data for the most stable conformers of the species studied. The fragment of the infrared spectrum of acetanilide in DMSO-d_6 solution is shown in Figure. 1.

The numerical values of the experimental IR data are compared with the theoretical ones in Table 1.

Fairly good agreement between the scaled theoretical and measured IR frequencies is observed. The mean deviation between them is 10 cm^{-1}. The largest differences between theoretical and experimental IR data correspond to the N-H stretching vibrations. They form a multiplet in the interval 3300 – 3080 cm^{-1}, because of the formation of strong hydrogen bonds mainly with DMSO solvent. The assignment of the experimental bands to the calculated normal modes in the C–H stretching region (3040–2800 cm^{-1}) is not obvious because there are fewer bands in the experimental spectrum than predicted by the calculations

Table 1. Theoretical (B3LYP/6-311+G(2df,p) and experimental (solvent DMSO-d_6) vibrational frequencies (cm^{-1}) and IR integrated intensities (A in $km.mol^{-1}$) of acetanilide

$\nu_{calc.}$	$\nu_{calc.}^{a}$	A_{calc}	Approximative description[b]	$\nu_{exp.}$	$A_{exp.}$
3622	3574	19.2	100 ν(N-H)	3301-3070	
3243	3200	5.5	99 ν(Ph-H)		
3189	3147	15.1	91 ν(Ph-H)		
3174	3133	20.1	86 ν(Ph-H)	3041	10.2
3165	3123	0.2	90 ν(Ph-H)		
3146	3104	12.7	100 ν(Ph-H)	3010	14.1
3114	3072	3.6	100 $\nu^{as}(CH_3)$	2977	8.8
3113	3072	15.7	100 $\nu^{as}(CH_3)$	2934	10.5
3042	3002	9.5	100 ν^{s} (CH_3)	2855	4.2
1750	1715	246.7	81 ν(C=O)	1686	127.5
1643	1610	43.6	53 ν^{Ph}(CC), 10 δ^{Ph}(CCH)	1617	45.7
1634	1601	37.7	55 ν^{Ph}(CC), 10 δ(HNC)	1599	34.3
1555	1524	292.3	42 δ(HNC), 15 ν(N-C), 10 δ^{Ph}(CCH)	1547	118.6
1531	1501	63.7	71 δ^{Ph}(CCH)	1495	51.3
1489	1460	12.5	95 $\delta(CH_3)$		
1470	1441	7.2	93 $\delta(CH_3)$		
1468	1439	125.0	58 ν(Ph-H), 15 δ(HNC)	1443	50.1
1400	1372	34.8	88 $\delta(CH_3)$	1372	32.1
1360	1333	8.3	76 ν(Ph-H)		
1338	1321	120.5	43 ν^{Ph} (CC), 35 ν(N-C)	1317	60.2
1265	1249	92.7	17 δ(HNC), 17 ν(Ph-N)	1263	35.9
1236	1219	37.0	18 ν(C-CH3), 17 ν(N-C), 15 ν(Ph-N)		
1206	1182	19.5	90 ν(Ph-H)	1177	20.4
1185	1169	0.9	79 ν(Ph-H)		
1114	1099	9.0	40 ν^{Ph} (CC), 33 ν(Ph-H)		
1054	1040	5.4	56 ν^{Ph} (CC)		
1053	1039	5.8	95 $\delta(CH_3)$		
1019	1006	9.1	77δ^{Ph}(CCC)		
1013[c]	1000	11.4	90 $\delta(CH_3)$		

[a] Scaled by 0.985[24]. [b] Vibrational modes: ν, stretching; δ, bendings. The numbers before the mode symbols indicate % contribution (10 or more) of a given mode to the corresponding normal vibration, according to the potential energy distribution. [c] Followed by 22 lower-frequency normal vibrations.

Table 2. Theoretical (B3LYP/6-311+G(2df,p) and experimental (solvent DMSO-d_6) vibrational frequencies (cm^{-1}) and IR integrated intensities (a in km mol^{-1}) of acetanilide anion.

$\nu_{calc.}$	$\nu_{calc.}{}^{a}$	A_{calc}	Approximative description[b]	$\nu_{exp.}$	$A_{exp.}$
3221	3175	4	99 ν(Ph-H)		
3159	3114	35	100 ν(Ph-H)		
3149	3104	73	99 ν(Ph-H)	3048	18.1
3119	3074	53	99 ν(Ph-H)	3008	16.2
3111	3067	17	99 ν(Ph-H)		
3101	3057	36	89 $\nu^{as}(CH_3)$		
3055	3012	42	100 $\nu^{as}(CH_3)$	2960	17.3
3008	2965	80	100 $\nu^{s}(CH_3)$	2915	14.5
1628	1603	63	59 $\nu^{Ph}(CC)$, 22 $\delta^{Ph}(CCH)$	1594	49.1
1576	1552	16	61 $\nu^{Ph}(CC)$, 15 $\delta^{Ph}(CCH)$,13 $\delta^{Ph}(CCC)$		
1570	1545	815	67 ν(C=O), 16ν(N-C)	1533	388.2
1508	1485	212	63 $\delta^{Ph}(CCH)$, 10 ν(Ph-N)	1480	99.3
1478	1455	4	88 $\delta(CH_3)$		
1472	1449	1	44 $\delta^{Ph}(CCH)$, 21 $\nu^{Ph}(CC)$		
1465	1443	30	67 $\delta(CH_3)$	1430	51.6
1398	1378	696	36 ν(N-C), 23 ν(Ph-N)	1385	219.7
1354	1335	1	92 $\delta(CH_3)$	1339	37.8
1339	1320	57	50 $\delta^{Ph}(CCH)$, 11 $\nu^{Ph}(CC)$		
1299	1280	59	54 $\nu^{Ph}(CC)$, 10 $\delta^{Ph}(CCH)$	1266	30.5
1238	1220	3	26 ν(Ph-N), 16 ν(N-C)	1216	32.7
1176	1159	36	60 $\delta^{Ph}(CCH)$	1165	19.1
1165	1148	3	78 δPh(CCH)	1129	2.2
1087	1072	9	50 δPh(CCH), 23 $\nu^{Ph}(CC)$		
1048[c]	1033	1	92 $\delta(CH_3)$, δ(OCN)		

[a]Scaled by 0.9858 [24]. [b] Vibrational modes: ν, stretching; δ, bendings. The numbers before the mode symbols indicate % contribution (10 or more) of a given mode to the corresponding normal vibration, according to the potential energy distribution matrix. [c] Followed by 24 lower-frequency normal vibrations.

The highest frequency experimental bands observed in the IR spectrum (3040–3000 cm^{-1}) are assigned to the aromatic C-H stretches, while the lower frequency bands are attributed to the methyl group motions. The ν(C-H) bands are of low intensity in both the experimental and theoretical spectra.

DFT calculations reproduce well the IR frequencies measured in DMSO of the Amide-I, Amide-II, Amide-III vibrations. The Amide-I mode (ν(CO)) is predicted to appear at 1715 cm^{-1} as a very intense band. Experimentally, a very strong band was detected at 1686 cm^{-1} in DMSO. In KBr pellet this band is downshifted strongly to 1665 cm^{-1} due to intermolecular hydrogen N–H…C=O bonding in the crystal [14]. The strong IR band observed at 1544 cm^{-1} was identified as Amide-II (the scissoring deformation δ(HNC)) in accordance with its scaled theoretical value of 1524 cm^{-1}. The stretching ν(N-C) strongly coupled with CC, denoted as Amide-III was predicted as a high intensity band at 1321 cm^{-1} and measured at 1317 cm^{-1} in the experimental spectra. The theoretical and experimental IR data for the acetanilide azanion are compared in Table 2.

As above we can find there a good agreement between experimental and scaled theoretical frequencies. The mean deviation between them is 9.1 cm^{-1} within the corresponding interval of 9–25 cm^{-1}, typical for DFT calculations of frequencies for series of anions [2-6]. The frequency isotopic shifts, resulting from the ^{15}N substitution, are also well reproduced (Table 3).

The conversion of acetanilide into the azanion results in very essential changes in the IR spectrum (Tables 1 and 2; Figure 1), *e.g.*:

- Essential decrease in the carbonyl stretching frequency ν(CO). There is no longer carbonyl band at the usual place. Its frequency decreases by: predicted 170 cm^{-1}, measured

153 cm^{-1}. The appearance of ν(CO) bands of acetanilide azanion at 1533 cm^{-1} corroborated the assignment reported by Ognyanova and coworkers [19] and agree qualitatively with assigned of the very strong band at 1549 cm^{-1} in IR spectrum of paracetamol dianion [30]. Incorrectly Liu *et al.* [31] assumed that the band at 1594 cm^{-1} in the IR spectrum of the complex containing deprotonated acetanilide ligand originates from $\nu_{C=O}$ in analogy to the spectrum of the acetanilides. A -8 cm^{-1} ^{15}N isotopic shift has been measured in DMSO for this band; the theory gives a -2 cm^{-1} value of the same sifts.

- Essential increase in the integrated intensity of the carbonyl band A_{CO}: predicted 3.3fold, measured 3 fold.
- Increase in C-N stretching frequency ν(C-N): predicted 57 cm^{-1}, measured 68 cm^{-1}. The shift of this the coordinate to higher frequency is obviously due to the significant shortening of the C-N bond, caused by the conversion of the acetanilide molecule into the azanion.
- Essential increase in the corresponding intensity $A_{C\text{-}N}$: predicted 5.8fold, measured 3.6 fold.
- Strong enhancement of the intensity of the aromatic skeletal bands of the phenylene ring 19 (Wilson's notation): predicted 3.3-fold, measured 2-fold.

Table 3. Theoretical (B3LYP/6-311+G(2df,p) end experimental (in DMSO) vibrational frequencies (cm^{-1}) of acetnalilide azanion-^{15}N and corresponding isotopic shifts.

Azanion		Azanion-^{15}N		$\Delta_{calc.}$	$\Delta_{exp.}$
$\nu_{calc.}$	$\nu_{exp.}$	$\nu_{calc.}$	$\nu_{exp.}$		
1603	1594	1602	1592	-1	-2
1552		1552		0	
1545	1533	1543	1525	-2	-8
1485	1480	1484	1478	-1	-2
1455		1455		0	
1449		1449		0	
1443	1430	1442	1430	0	0
1378	1385	1362	1373	-16	-12
1335	1339	1332	1334	-2	-5

Structural analysis of the species studied

According to X-ray diffraction experimental data the dihedral angle between the phenyl ring and amide group planes in the monoclinic crystal of acetanilide is 43.4° [26]. According to the calculations in the most stable conformers of the isolated molecule these groups are planar. The same groups in the isolated azanion have been predicted to be again planar. The theoretical and experimental bond lengths and angles in the acetanilide and its azanion are listed in Table 4.

Table 4. Theoretical (B3LYP/6-311+G(2df,p)) and experimental bond lengths R (Å) and bond angles A (°) in the acetanilide molecule and its azanion.

	Molecule			Anion	
	Experimental[a]	Theoretical	Δ[b]	Theoretical	Δ[c]
Bond lengths					
R(C^1,C^2)	1.394	1.397	0.003	1.421	0.024
R(C^2,C^3)	1.385	1.390	0.005	1.390	0.000
R(C^3,C^4)	1.383	1.389	0.006	1.393	0.004
R(C^4,C^5)	1.390	1.390	0.000	1.396	0.006
R(C^5,C^6)	1.378	1.385	0.007	1.384	-0.001
R(C^1,N^{12})	1.409	1.409	0.000	1.376	-0.033
R(N^{12},C^{14})	1.348	1.374	0.026	1.338	-0.036
R(C^{14},O^{15})	1.222	1.216	-0.006	1.252	0.036
R(C^{14},C^{16})	1.505	1.516	0.011	1.534	0.018
Bond angles					
A(C^1,C^2,C^3)	119.6	119.3	-0.3	121.1	1.7
A(C^4,C^3,C^2)	121.2	121.4	0.2	121.8	0.5
A(C^5,C^4,C^3)	120.4	119.1	-1.3	118.1	-1.0
A(C^6,C^5,C^4)	120.5	120.2	-0.3	120.7	0.5
A(N^{12},C^1,C^6)	116.9	117.1	0.2	116.3	-0.9
A(C^{14},N^{12},C^1)	127.5	129.5	2.0	122.6	-6.9
A(N^{12},C^{14},O^{15})	123.3	124.0	0.7	130.2	6.2
A(C^{16},C^{14},N^{12})	115.5	114.6	-0.9	113.4	-1.3

[a] See Ref. [26]. [b] Algebraic deviations (Å, degrees) between experimental and theoretical values. [c] Algebraic deviations (Å, degrees) between theoretical values of the anion and molecule.

As seen, there is a good agreement between the experimental and the theoretical values. The largest deviation from 0.026 Å is in bond N^{12}-C^{14} and can be associated with the formation of hydrogen bonds in the solid state. The mean absolute deviations (m.a.d.) between theoretical and experimental bond lengths and angles of acetanilide molecule are 0.006 Å and 0.07, respectively. This result leads us to believe that the theoretical bonds lengths and angle for the acetanilide anion are also reliable. The most significant changes caused by the conversion molecule azanion take place both at the azanionic center and next to it, with agrees the data for other azanions [2,4]. They are strong shortening of the Ph-N and N-C and bonds, strong lengthening of the C=O and C-CH_3 bonds.

The net electronic charges q of the fragments of the species studied are as follows:

	C_6H_5	NH/N^-	$COCH_3$
q in the molecule	0.098	0.012	-0.110
q in the azanion	-0.206	-0.339	-0.455

The charge change values Δqi= qi (anion) - qi (molecule) are usually quite informative in showing the distributions of the new charges in anions [2-4,30]. According to the present calculations, the new (azanionic) charge is distributed as follows: -0.304 e^- and -0.346 e^- are delocalized over the phenyl and acetyl groups and -0.349 e^- of its remained localized at the azanionic centre.

CONCLUSION

The spectral and structural changes, caused by the conversion of the acetanilide molecule into the corresponding azanion have been studied by IR spectra DFT method at B3LYP/6-311+G(2df,p) level.

A comparison of calculated with measured infrared data can be used as a test for the reliability of the structural predictions for various molecules and anions of this and similar types. These predictions can be very useful in cases of molecules and ions for which experimental structural parameters are inaccessible or unknown. IR spectral changes, which take place as a result of the conversion of molecule into azanion, were adequate predicted by same theoretical method.

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ИЧ СПЕКТРАЛНИ И СТРУКТУРНИ ПРОМЕНИ ПРИЧИНЕНИ ОТ ПРЕВРЪЩАНЕТО НА АЦЕТАНИЛИДА В АЗАНИОН

Е. А. Велчева*, З. И. Главчева, Б. А. Стамболийска

Лаборатория „Структурен органичен анализ”, Институт по органична химия с център по фитохимия, Българска академия на науките, ул. „Акад. Г. Бончев”, бл.9, 113 София

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Структурите на азаниона на ацетанилида и на неговия ^{15}N белязан аналог са изследвани с помощта на ИЧ спектри и ТФП изчисления, използвайки B3LYP функционал и 6-311+G(2df,p) базисен набор. Намерено е добро съответствие между теоретичните и експерименталните вибрационни характеристики на изследваните частици. Превръщането на молекулата ацетанилид в азанион предизвиква 150 cm^{-1} понижение на карбонилната валентна честота, трикратно увеличение на интегралната интензивност на съответната ИЧ ивица и други съществени спектрални промени. Според изчисленията, структурните промени в пространствената структура, причинени от това превръщане, са *при* и *непосредствено до* азанионния център. Новият (азанионен) заряд се разпределя както следва: -0.304 e$^-$ и -0.346 e$^-$ са делокализирани върху фенилната и ацетилната групи и 0.349 e$^-$ от него остават локализирани при азанионния център.