Bulgarian Chemical Communications, Volume 46, Special Issue A (pp. 157 – 163) 2014

IR spectral and structural changes, caused by the conversion of 4-cyanobenzenosulfonamide into azanion

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Received May 28, 2014; Revised July 14, 2014

Dedicated to Acad. Dimiter Ivanov on the occasion of his 120th birth anniversary

A combined IR experimental/DFT computational approach has been applied to follow the spectral and structural changes, caused by the conversion of 4-cyanobenzenesulfonamide into azanion. The conversion has shown a weak effect on the cyano stretching band $\nu_{C\equiv N}$ and strong effects on both $\nu^{as}_{SO_2}$ and $\nu^{S}_{SO_2}$ stretching bands. According to the computations, the strong structural changes, caused by the conversion, take place *at* and *next to* the azanionic center. The new (azanionic) charge is distributed as follows: 0.08 e^-, 0.25 e^- and 0.10 e^- are delocalized over the cyano, phenilene and sulfonyl groups, respectively, and 0.57 e^- of it remain localized in the azanionic center.

Key words: IR spectra, DFT/B3LYP, 4-cyanobenzenesulfonamideamide, azanion

INTRODUCTION

Sulfonamides (SA) are well known for their various biological activities: antibacterial, diuretic, antidiabetic etc. [1]. The unsubstituted in sulfamide group aromatic/heterocyclic SA are known as inhibitors of the zinc-enzyme Carbonic anhydrase (CA) with diuretic activities, hypoglycemic activity and anticancer properties [2,3]. This enzyme catalyzes the reversible hydration of carbon dioxide and both meta- and para- substituted SAs are specific and potent inhibitors of CA. The inhibition mechanism seems to be mainly connected with the generation of an electrostatic field of the zinc ion which favors the correct orientation of the SO_2NH_2 group and its anticipated deprotonation. So, the inhibitory action is caused by the binding of the sulfamide anion to the Zn^{2+} of the enzyme, mimicking the bicarbonate anion in the transition state [3-5]. Due to their pharmacology applications and widespread use in medicine, these compounds have gained attention in many fields of drug chemistry.

4-Cyanobenzenesulfonamide is a representative of the benzenesulfonamides with primary sulfonamide group. 4-Cyanobenzenesulfonamide was first prepared almost 120 years ago by Remsen et al. [6] using a multistep synthesis, starting with 4-(aminosulfonyl)benzoic acid. There is a recent study of the title compound by Camí and coworkers [7]. They have synthesized 4-cyanobenzenesulfonamide and its copper complex and reported their UV, IR and Raman spectra and B3LYP calculations. The structure and IR spectra of 4-cyanobenzenesulfonamide azanion itself have never been studied experimentally or theoretically. The conversions of neutral molecules into radical anions, carbanions, azanions, etc., are accompanied with essential changes in the vibration spectra. So, these changes are very informative for the structural variations that result from the above conversions [8-11].

The purpose of the present investigation is to follow the spectral and structural changes, caused by the conversion of 4-cyanobenzenesulfonamide molecule into the corresponding azanion on the basis of both DFT computations and IR spectroscopic experiments.

EXPERIMENTAL

The sample of p-cyanobenzenesulfonamide (Manchester Organic Limited, spectroscopic grade) was used without any additional purification. Its azanion was prepared by adding dimethyl sulfoxide (DMSO/DMSO-d_6) solutions of the parent compound to excess of dry $CD_3O^-Na^+$ under argon, and collecting the clear azanion solution with a syringe-filter. We prepared the sample of $CD_3O^-Na^+$ itself by reacting CD_3OD (Fluka, 99% at. enrichment) with Na and evaporating the excess of methanol *in vacuo.* p-Cyanobenzenesulfonamide reacted with

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$CD_3O^-Na^+$ to form the azanion in DMSO/DMSO-d_6 promptly (within 1-2 min) and practically completely: no bands of the parent compound were seen in the spectra after metalation.

The IR spectra are recorded on a Brucker Tensor 27 FTIR spectrophotometer in a CaF_2 cell of 0.129 mm path length(for DMSO/ DMSO-d_6 solutions), a KBr cells of 0.6 mm path length (for saturated $CDCl_3$ solutions) and in KBr and CsI disks, at a resolution of $1cm^{-1}$ and 64 scans.

COMPUTATIONS

The quantum chemical calculations were performed using the Gaussian 09 package [12] on a MADARA grid. 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, Yang and Parr [13,14], adopting 6-31++G(d,p), 6-311+G(2df,p) and aug-cc-pVTZ basis sets. The stationary points found on the molecular potential energy hypersurfaces were characterized using standard harmonic vibrational analysis. The absence of imaginary frequencies confirmed that the stationary points corresponded to minima on the potential energy hypersurfaces. In order to check statistically which basis set performed agrees best with the experimental data for the species studied, we have treated the correlations between their theoretical and experimental IR frequencies. The comparison has shown that the B3LYP/6-311+G(2df,p) IR data correlate best with the experimental ones. For a better correspondence between experimental and calculated values, we modified the results using the empirical scaling factors [15].

RESULTS AND DISCUSSION

Energy analysis

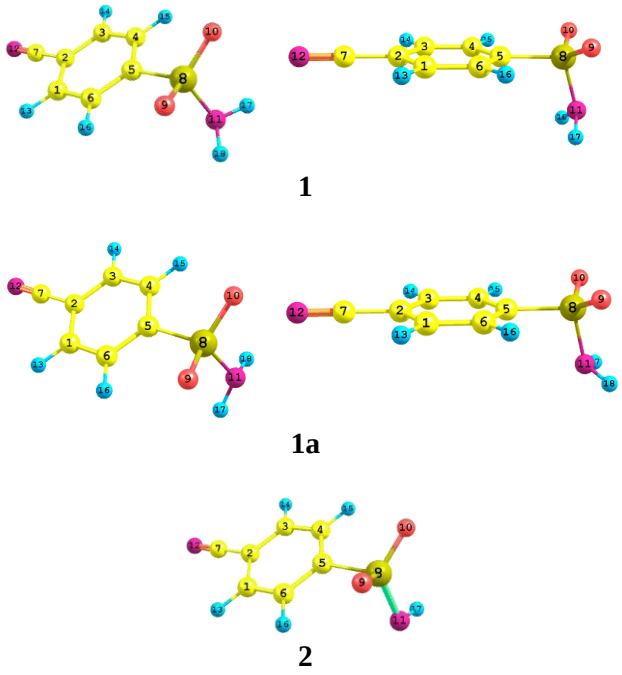
The full conformational search on the potential energy surface of the molecule and azanion of 4-cyanobenzenesulfonamide allowed the identification of two different minima of the molecule, all of them bearing the sulfamide nitrogen atom placed in the perpendicular orientation relatively to the aromatic ring and differing from each other in the orientation of the amide hydrogen atoms and one minimum of the azanion. The conformers of the species studied are shown in Fig. 1 and their energies are compared in Table 1. The deprotonation energy of a given Bröensted acid can be defined [16,17] (and references therein) as

$$E^D = E^{anion}_{corr} - E^{molecule}_{corr}$$

(for the most stable conformers of these species). Georgieva and Velcheva [16] have found that E^D (B3LYP/6-31++G(d,p)) values correlate fairly well with pKa's of Bröensted acids, containing cyano or carbonyl groups, measured in DMSO solvent, according to correlation equation:

$$pKa(DMSO)=0.11507\ x\ E^D-150.04(kJ/mol)\,.$$

So, having in mind E_{corr} of 1 and 2 in Table 1, we can estimate pKa (DMSO) of 4-cyanobenzensulfonamide near 9.4. Hence, 4-cyanobenzensulfonamide should be a moderately weak N-H acid, (for comparison literature data for pKa (DMSO) of benzenesulfonamide is 16.1 [18]).



1

1a

2

Fig. 1. B3LYP/6-311+G(2df,p) optimized structures of the species studied.

Spectral analysis

Theoretical and experimental IR data for 4-cyanobenzenesulfonamide molecule are compared in Table 2. We can see there is a good agreement between experimental and scaled theoretical frequencies. M.a.d between them is 12.9 cm^{-1}, which value lies within the interval of 9-20 cm^{-1}, typical for the DFT calculations for molecules containing

cyano or carbonyl groups [17,19-23] (and references therein). We include in Table 2 the frequencies $\nu^{as}_{NH_2}$ and $\nu^{s}_{NH_2}$ measured in $CDCl_3$, as the stretching frequencies of –XHn groups (X= O, N, etc.), measured in DMSO, are strongly underestimated, and the bending ones strong –XHn - - - $O=S(CH_3)_2$ hydrogen bonds, which effects can be estimated only qualitatively

Table 1. Zero-point vibrational energy (ZPVE) corrected total energies ($E^{corr.}$ in hartree) of 4-cyanbenzenesulfonamide molecule **1** and of its azanion **2**, as well as their differences (ΔE in kJ/mol).

Species	B3LYP 6-31++G(d,p)		B3LYP/aug-cc-pVTZ		B3LYP/6-311+(2df,p)	
	$E^{corr.}$	ΔE	$E^{corr.}$	ΔE	$E^{corr.}$	ΔE
Molecule **1**	-928.322889	0.00	-928.679457	0.00	-928.539333	0
Molecule **1a**	-928.320810	5.46	-928.678335	2.95	-928.538131	3.16
Azanion **2**	-927.795230	1385.37	-928.138421	1420.49	-928.012712	1382.64

Table 2. Theoretical B3LYP/6-311+(2df,p) and experimental (in DMSO/DMSO-d_6) IR frequencies (ν in cm^{-1}) and integrated intensities (A in *km/mol*) of 4-cyanobenzenesulfonamide molecule.

	B3LYP/6-311+(2df,p)				Experimental data
No.	ν	**A**	ν^a	**Approximate description**[b]	ν [c]
1	3642	57.6	3595	$\nu^{as}_{NH_2}$	3456[d]
2	3527	61.9	3481	$\nu^{s}_{NH_2}$	3350[d]
3	3220	2.2	3178	ν_{PhH}	3153[d]
4	3218	0.0	3177	ν_{PhH}	-[e]
5	3204	1.0	3162	ν_{PhH}	3096[d]
6	3203	0.0	3162	ν_{PhH}	-[e]
7	2334	26.1	2303	$\nu_{C\equiv N}$	2232 m
8	1628	0.2	1607	ν_{CC}, δ_{PhH}	1601 sh
9	1594	2.1	1573	ν_{CC}, δ_{PhH}	1570 broad
10	1574	34.0	1554	$\delta^{sc}_{NH_2}$	1554 sh
11	1514	6.0	1495	δ_{PhH}, ν_{CC}	1491 m
12	1419	20.6	1400	δ_{PhH}, ν_{CC}	1397 m
13	1371	175.7	1353	$\nu^{as}_{SO_2}$, $\delta^{rock}_{NH_2}$, ν_{CC}	1342 vs
14	1327	2.3	1310	ν_{PhH}, ν_{C-S}, δ_{CCC}	-[e]
15	1320	20.5	1303	ν_{PhH}, δ_{CCC}	1282 m
16	1215	1.6	1199	ν_{PhH}, ν_{C-CN}	1197 sh
17	1201	1.3	1186	δ_{PhH}, ν_{C-CN}	1185 m
18	1156	216.7	1141	$\nu^{s}_{SO_2}$, $\delta^{sc}_{NH_2}$, ν_{C-S}, δ_{CCC}	1165 vs
19	1131	4.3	1116	δ_{PhH}	1111 vw
20	1093	26.6	1079	ν_{C-S}, δ_{PhH}	1095 m
21	1071	1.2	1057	$\delta^{rock}_{NH_2}$	-[e]
22[d]	1028	4.7	1015	δ_{CCC}	-[e]

[a] Scaled by 0.9686 [15].[b] Vibrational modes: ν, stretching; δ, bendings. [c] Relative intensities: vs, very strong; s, strong; m, moderate; w, weak; vw, very weak; sh, shoulder. [d] Solvent $CDCl_3$. [e] These bands were not detected in the experimental spectrum. [d] Followed by 26 lower-frequency normal vibrations.

Table 3. Theoretical B3LYP/6-311+(2df,p) and experimental (in DMSO/DMSO-d_6) IR frequencies (ν in cm^{-1}) and integrated intensities (A in *km/mol*) of 4-cyanobenzenesulfonamide azanion.

	B3LYP/6-311+(2df,p)				Experimental data
No.	ν	**A**	ν^a	**Approximate description[b]**	ν [c]
1	3496	6.2	3451	ν_{NH^-}	-[d]
2	3204	4.4	3162	ν_{PhH}	-[d]
3	3203	7.1	3161	ν_{PhH}	-[d]
4	3178	9.9	3137	ν_{PhH}	3076 vw
5	3176	9.9	3135	ν_{PhH}	-[d]
6	2301	225.7	2271	$\nu_{C\equiv N}$	2227 s
7	1612	102.2	1592	ν_{CC}, δ_{PhH}	1593 m
8	1574	3.2	1554	δ_{PhH}, ν_{CC}	-[d]
9	1503	10.3	1483	δ_{PhH}, ν_{CC}	1487 m
10	1417	7.5	1398	δ_{PhH}, ν_{CC}	1396 w
11	1326	0.5	1309	δ_{CCC}	-[d]
12	1313	0.4	1296	ν_{PhH}	1295 vw
13	1248	220.2	1231	$\nu^{as}_{SO_2}$, δ_{CNH^-}, δ_{PhH}	1228 vs
14	1213	15.2	1197	ν_{C-CN}, δ_{PhH}, δ_{CC}	1190 vw
15	1190	11.5	1174	δ_{PhH}	1177 vw
16	1132	167.5	1117	$\nu^{s}_{SO_2}$, δ_{PhH}, δ_{SNH}	1134 vs
17	1116	24.4	1102	δ_{PhH}, δ_{CNH^-}	-[d]
18	1091	46.8	1077	δ_{CNH^-}, ν_{C-S}	1096 s
19	1077	113.6	1063	δ_{SNH}, δ_{CCC}, ν_{C-S}	-[d]
20[e]	1029	2.7	1015	δ_{CCC}	-[c]

[a] Scaled by 0.9686 [15]. [b] Vibrational modes: ν, stretching; δ, bendings. [c] Relative intensities: vs, very strong; s, strong; m, moderate; w, weak; vw, very weak. [d] These bands were not detected in the experimental spectrum. [e] Followed by 25 lower-frequency normal vibrations.

within the Onzeger's approach [24]. There are no peculiarities of the cyano stretching band: moderately high frequency $\nu_{C\equiv N}$ and intensity $A_{C\equiv N}$, as the cyano and phenylene groups are in resonance. The frequencies of the strongest in the spectrum sulfonyl stretching bands $\nu^{as}_{SO_2}$ and $\nu^{s}_{SO_2}$ measured in DMSO agree well with those measured in solid state (Fig. 2 curves **a** and **b**). Its frequencies of 1342 cm^{-1} and 1165 cm^{-1} are higher with 37 cm^{-1} (sum) than corresponding values of sulfanilamide (solvent DMSO-d_6) [9] due to electron-withdrawing effect of cyano group.

We compare in Table 3 theoretical and experimental IR data for the azanion of 4-cyanobenzenesulfonamide (2 in Fig. 1). The agreement between experimental and scaled theoretical frequencies is essentially better than above. M.a.d between them is 10.1 cm^{-1} only, close to the lower limit of the corresponding integral of 9-25 cm^{-1}, typical for DFT calculations of vibrational frequencies for anions containing cyano or carbonyl groups [17, 19-23] (and references therein). The experimental IR spectra of azanion and molecule (in DMSO/ DMSO-d_6) are compared in Fig. 2 (curves c and b).

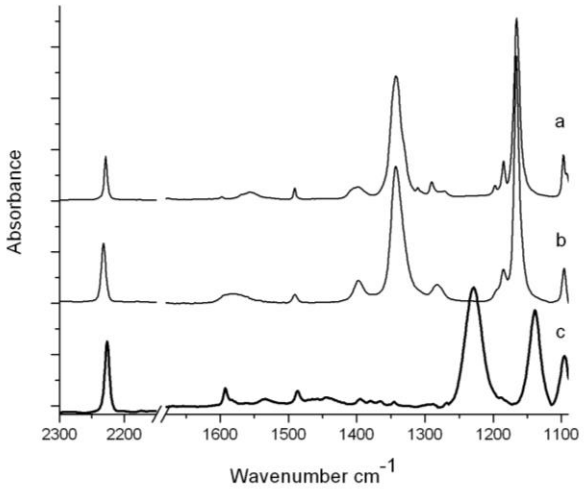


Fig. 2. Experimental spectra of 4-cyanobenzenesulfonamide (**a** in KBr; **b** in DMSO/DMSO-d_6) and its azanion **c** (0.1 mol^{-1} solutions in DMSO/DMSO-d_6).

The following spectral changes take place as a result of the conversion of 4-cyanobenzene-sulfonamide into azanion:

i) According to the computations, both $\nu^{as}_{SO_2}$ and $\nu^{s}_{SO_2}$ undergo essential frequency decreases, which sum is: predicted 146 cm^{-1}, measured 145 cm^{-1}. The latter value is rationally larger than the corresponding values for other cases of molecule-azanion pairs, containing additional electron-withdrawing groups (compound, ν_{SO_2} sum): o-sulfobenzimide (saccharin), 93 cm^{-1} [25]; o-sulfothiobenzimide (thiosaccharin), 60 cm^{-1} [26] and similar than in sulfanilamide, 140 cm^{-1} [9].
ii) The computational method used predicts only qualitatively the changes in the cyano stretching band characteristics, viz.: $\nu_{C\equiv N}$ decreases: predicted 32 cm^{-1}, measured 5 cm^{-1} only.
iii) According to the calculations, in the azanion a new δ_{CNH^-} mode takes essential parts in vibrations Nos. 13, 18, and 19 (Table 3).

Structural analysis

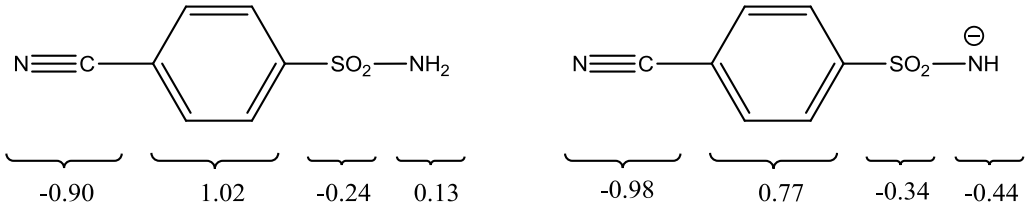
We can see in Table 4 a good agreement between experimental [7] and theoretical bond lengths of 4-cyanobenzenesulfonamide molecule **1**: the mean absolute deviation between them is 0.019 Å. There are no experimental structural data for 4-cyanobenzenesulfonamide azanion. According to our computations, the conversion of the molecule into azanion causes certain essential steric structure variations (Table 4). It is seen in there that the largest bond length changes should take place at the azanionic center (shortening of the S^8-N^{11} bond by 0.106 Å) and next to it (lengthening of the C^5-S^8 bond by 0.037 Å) etc. The same rule is also valid for the corresponding bond angles changes.

Table 4. Selected B3LYP/6-311+G(2df,p) bond lengths R (Å), bond angles A(degrees) and dihedral angle D(degrees) of 4-cyanobenzenesulfonamide molecule **1** and its azanion **2**.

Indices[a]	Molecule		Azanion	∇^c
	Theor.	Exper.[b]		
R(1,2)	1.403	1.383	1.409	0.006
R(1,6)	1.390	1.387	1.386	-0.004
R(2,3)	1.403	1.383	1.404	0.001
R(2,7)	1.433	1.462	1.429	-0.004
R(3,4)	1.390	1.387	1.391	0.001
R(4,5)	1.395	1.377	1.398	0.003
R(5,6)	1.394	1.377	1.401	0.007
R(5,8)	1.792	1.777	1.829	**0.037**
R(7,12)	1.158	1.130	1.162	0.004
R(8,9)	1.444	1.420	1.464	0.020
R(8,10)	1.444	1.420	1.473	0.029
R(8,11)	1.667	1.601	1.561	**-0.106**
A(4,5,8)	119.3	118.7	121.1	1.8
A(5,8,9)	107.3	107.4	102.4	-4.9
A(5,8,10)	107.3	107.4	103.1	-4.2
A(5,8,11)	103.4	108.7	106.0	2.6
A(9,8,10)	122.7	119.6	116.8	-5.9
A(9,8,11)	107.3	106.6	110.7	3.4
D(6,5,8,9)	-22.6	-26.4	-45.8	**-23.2**
D(6,5,8,11)	90.6	88.7	70.3	**-20.3**
D(10,8,11,17)	2.9	-	26.1	**-23.2**

[a] Atomic numbering, according to Figure 1. [b] See Ref. [7]. [c] Algebraic deviations (Å, degrees) between theoretical and experimental values of the anion and molecule. The largest values are given in bold.

The changes in the *electronic structure* of 4-cyanobenzenesulfonamide, caused by its conversion into azanion, can be demonstrated on the basis of net electronic charges. Scheme 1 contains values of net electric charges q_i over fragments of molecule **1** and azanion **2** studied. The electric charge *changes* $\Delta q_i = q_i^{anion} - q_i^{molecule}$ are usually quite informative to demonstrate the distribution of the new (carbanionic, azanionic, etc.) charge between individual fragments of anions [8,9,17,27,28] (and references therein). According to our calculations, the anionic charge in 4-cyanobenzenesulfonamide azanion is distributed, as follows: 0.08, 0.25 and 0.10 e^- are delocalized over the cyano, phenylene and sulfonyl groups, respectively, and 0.57 e^- of it remains localized in the azanionic center.



1 **2**

Scheme 1. Mulliken net electric charger q_i over fragments of molecule **1** and azanion **2** of 4-cyanobenzenesulfonamide.

CONCLUSION

We found on the basis of both experimental and computational IR data that the effect of the conversion of 4-cyanobenzenesulfonamide into azanion on the cyano group was weak and was essential on the pharmacological important sulfonamide group. This statement was confirmed by the analysis of both steric and electronic structures, computed for the species studied.

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ИЧ-СПЕКТРАЛНИ И СТРУКТУРНИ ПРОМЕНИ, ПОРОДЕНИ ОТ ПРЕВРЪЩАНЕТО НА 4-ЦИАНОБЕНЗЕНСУЛФОНАМИД В АЗАНИОН

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Постъпила на 28 май 2014 г.; Коригирана на 14 юли 2014 г.

(Резюме)

Приложен е комбиниран ИЧ експериментален/DFT теоретичен подход за проследяване на спектралните и структурни промени, породени от превръщането на 4-цианобензенсулфонамида в азанион. Ефектът на превръщането се проявява слабо върху валентното трептение на нитрилната група $\nu_{C\equiv N}$ и силно върху двете валентни трептения на сулфонамидната група $\nu^{as}_{SO_2}$ и $\nu^{s}_{SO_2}$. Според изчисленията, превръщането в азанион поражда значителни промени в структурата *при* и *непосредствено до* азанионния център. Според нашите изчисления новият (азанионен) заряд се разпределя както следва: 0.08 e^-, 0.25 e^- и 0.10 e^- са делокализирани съответно върху циано, фенилен и сулфонилната групи и 0.57 e^- от него остават локализирани при азанионния център.