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Experimental and DFT studies on the IR spectral and structural changes arising from the conversion of 4-amino-N-[amino(imino)methyl] benzenesulfonamide (sulfaguanidine) into azanion

A. Popova*, B. Stamboliyska, E. Velcheva

Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 9, 1113 Sofia, Bulgaria

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

The structure of 4-amino-N-[amino(imino)methyl] benzenesulfonamide (sulfaguanidine) and of its azanion have been studied on the basis of both infrared spectra and DFT calculations. A good agreement has been found between the theoretical and experimental vibrational characteristic of the particles studied. The theoretical method used gives a good description of the strong spectral changes caused by the conversion of the sulfaguanidine molecule into the corresponding azanion. The structural changes which accompany this conversion take place *at* and *next to* azanionic centre. According to the present calculations, the new (anionic) charge of azanion is distributed, as follows: -0.07 e^-, -0.37 e^- and -0.56 e^- over the amino group, phenylene ring and sulfonylguanidine fragment, respectively.

Key words: sulfaguanidine, azanion, IR, DFT

INTRODUCTION

4-Amino-*N*-[amino(imino)methyl]benzene-sulfonamide (sulfanilylguanidine, sulfaguanidine, SG) is the first sulfanilamide antimicrobial agent that is used to treat enteric infections such as bacillary dysentery. In April, 1940, Roblin *et al.* [1] presented the synthesis and physical properties of sulfanilylguanidine to the Division of Medicinal Chemistry at the meeting of the American Chemical Society. In September, 1940, Marshall, Jr., *et al.* [2] published a report of their experiments with sulfanilylguanidine. They had studied its antibacterial properties and its absorbability when given orally and intra-peritoneally. Although fairly soluble in water, sulfanilylguanidine is poorly absorbed from the intestinal tract, but it is a very effective antimicrobial agent.

The crystalline forms of sulfaguanidine have been studied extensively [3-8]. Yang and Guillory [5] found four polymorphic forms and discuss the possibilities of the system of hydrogen bonds. The crystal structure of sulfaguanidine monohydrate [6,7] and molecular structure of anhydrous sulfaguanidine is defined by means of X-ray diffraction [8].

The infrared (IR) spectra of SG in the solid state together with the main band assignments were reported long time ago [9,10] Trius using infrared spectroscopy for the identification of sulfonamide drugs [11]. The most recent IR spectroscopic investigation, complemented by theoretical studies of the SG has been reported by Chandran et.al. [12]. However, this investigation is incomplete, as only one tautomeric form (imino) was examined. It is known from NMR spectroscopic [9,13] and X-ray studies [6-8] that the preferred form assumed by the molecule of SG is the symmetrical structure (amino form).

Neither the IR spectra nor structure of sulfa-guanidine azanion have been studied theoretically or experimentally. 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 [14-18]. The purpose of the present investigation is to follow the spectral and structural changes, caused by the conversion of sulfaguanidine molecule into the corresponding azanion on the basis of both DFT computations and IR spectroscopic experiments.

EXPERIMENTAL AND COMPUTATIONS

The sulfaguanidine anion (counter ion Na+) was prepared by adding 0.05 and 0.2 mol/l DMSO/ DMSO-d_6 solutions of the parent sulfaguanidine to

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

equimolar quantities of dry alkali-metal methoxides -d_0 and -d_3 under argon. The conversion was practically complete (no bands of the parent compound were seen in the spectra after metalation).

The IR spectra were measured on a Bruker Tensor 27 spectrophotometer in a CaF_2 cell of 0.13 mm path length for DMSO/DMSO-d_6 solutions and in KBr disk, at a resolution of 1 cm^{-1} and 64 scans.

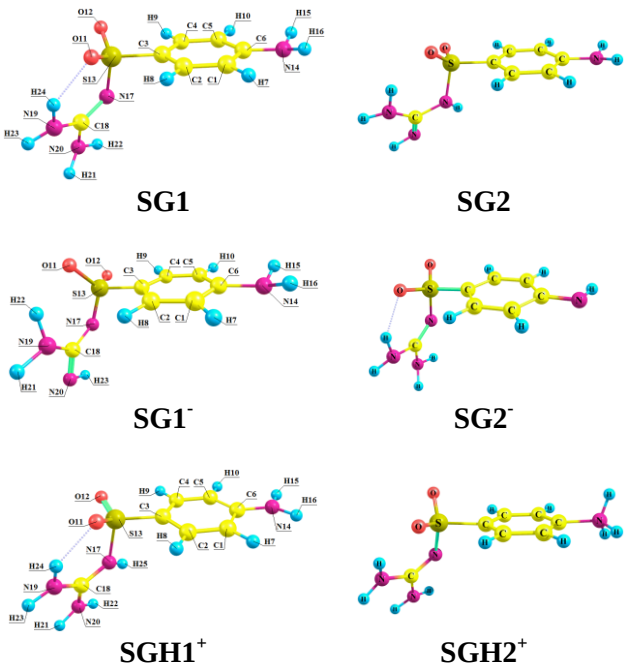
The quantum chemical calculations were performed using the Gaussian 09 package [19]. The geometry optimizations of the structures investigated were done without symmetry restrictions, using density functional theory (DFT). We employed B3LYP hybrid functional, which combines Becke's three-parameter nonlocal exchange with the correlation functional of Lee *et al.* [20,21], adopting 6-31+G* and 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 [22]. For a better correspondence between experimental and calculated values, we modified the results using the empirical scaling factors [23].

RESULTS AND DISCUSSION

Energies and conformational isomers

The sulfaguanidine molecule can exist as two tautomers, SG1 and SG2 which have its guanidine group in amino and imino form, respectively. All tautomers of sulfaguanidine and its protonated and deprotonated forms have different conformers resulting from rotation about C-S, S-N and N-C bonds. After a systematic conformation search on the B3LYP/6-31+G* potential energy of studied species, four different minima for molecule and six – for anion and cation are located. The structure of the most stable conformers were reoptimized at B3LYP/6-311(2df,p)G** and can be seen in Scheme 1; their total energies are compared in Table 1. The following comments can be made on the basis of the corresponding energy values:

- The tautomer SG1 is predicted to be more stable than SG2 one by more than 40 $kJ.mol^{-1}$. According to Minkin *at al.* [24] prototropic conversions are probable in case when the energy differences between the initial and the final structure do not exceed 25 $kJ.mol^{-1}$, with activation barrier not higher than 105 $kJ.mol^{-1}$. As it could be seen in Table 1 the energy difference is larger in the present case, and convinces that only SG1 should be expect to exist in real system. The presence of the same amino tautomer SG1 was established by crystallographic analysis [6,8] and experimental NMR spectral data in DMSO [9]. In recently published DFT vibrational analysis, Chandran and co-workers [12] computed only imino SG2 structure, which is less stable.
- The anion $SG1^-$ is the most stable among the possible anionic isomers, obtained through elimination of a proton from the guanidine group and with the 45 $kJmol^{-1}$ more stable than anion $SG2^-$ obtained through elimination of a proton from amino group.
- SG1H+ protonated at the guanidine group is the significantly more stable protonated isomer. The other isomer protonated at the N atom connected with phenyl ring highly improbable in gas state.



Scheme 1. B3LYP/6311+G(2df,p) optimized structures of the tautomers of sulfaguanidine molecule SG1 and SG2 and their protonated and deprotonated species.

The deprotonation energy (E^D) of a given species can be calculated as a difference between ZPVE-corrected energies of the most stable conformer of this species and of the corresponding deprotonated form. So, for species studied we can calculate from the data in Table 1:

Table 1. Total E_{tot} (in hartree) and relative E_{rel} (in kJ/mol) energies of sulfaguanidine molecule, its protonated and deprotonated species.

Species[a]	B3LYP/6-31+G*		B3LYP/6-311+G(2df,p)	
	E_{tot}	E_{rel}	E_{tot}	E_{rel}
SG1	-1040.41404		-1040.66028	
SG2	-1040.39780	42.55	-1040.64383	43.19
$SG1H^+$	-1040.79436		-1041.04101	
$SG2H^+$	-1040.75752	96.72	-1041.00436	96.20
$SG1^-$	-1039.85858		-1040.10438	
$SG2^-$	-1039.84153	44.74	-1040.08710	45.36

[a] Numbering according Scheme 1.

E^D of the sulfaguanidine:

$$E^{D}_{SG1} = 1459.52\ kJ/mol$$

E^D of the protonated sulfaguanidine:

$$E^{D}_{SG1H^+} = 999.60\ kJ/mol$$

The E^D values are related qualitatively with the acidities of the C–H, C–N etc. acids in DMSO and other solvents (lower E^D, higher acidity, lower pKa's). In the present case the above E^D value are also in a qualitative agreement with the experiment: the protonated sulfaguanidine is a strong acid (pK_a=2.75 [25]) and sulfaguanidine itself is a weak acid (pK_a=12.1 [26]).

Spectral analysis

The theoretical and experimental IR data, measured in DMSO solvent for the sulfaguanidine molecule are compared in Table 2. We can see there a good agreement between experimental and scaled theoretical frequencies. The mean absolute deviation between them is nearly 13 cm^{-1}.

The largest differences between theoretical and experimental IR data correspond to the NH_2 stretching vibrations. The calculations predict that the highest frequency band (3572 cm^{-1}) corresponds to the asymmetric deformation of amino group, the following frequencies (3561 cm^{-1}, 3560 cm^{-1}) correspond to the asymmetric NH_2 modes of guanidine structural motif, whereas the other ones (3464 cm^{-1}, 3463 cm^{-1}, 3387 cm^{-1}) are assigned respectively to the symmetric ones. The measured amino frequencies are significantly lower than theoretically predicted ones, due to the formation of strong hydrogen bonds between the sulfaguanidine molecules and DMSO-d_6 solvent. The theory predicted well the low intensities of the ν(PhH) bands. The stretching ν(NC) strongly coupled with deformation vibrations of δ(NH_2) of guanidine fragment is predicted to appear at 1626 cm^{-1} as a very intense band. Experimentally, a strong band was detected at 1640 cm^{-1}. Deformation vibration of the amino group is predicted as pure in 1607 cm^{-1} and found at 1600 cm^{-1}. The strong bands of the $\nu^{as}(SO_2)$ and $\nu^{as}(SO_2)$ frequencies, appear at 1269 $cm^{-1}$and 1137cm^{-1}, respectively. For comparison the corresponding bands of the saccharin molecule have been found at 1326 cm^{-1} and 1177 cm^{-1} (in DMSO solvent) [27] and we have found those of sulfanilamide molecule at 1317 cm^{-1} and 1153 cm^{-1} (in DMSO solvent) [16].

The theoretical and experimental IR data for the sulfaguanidine anion are compared in Table 3. As above we can find there a good agreement between experimental and scaled theoretical frequencies. The mean deviation between them is 13 cm^{-1} within the corresponding interval of 9-25 cm^{-1}, typical for DFT calculations of frequencies for series of carbanions [28,29], azanions [14] and oxyanions [15] (and references therein). The conversion of sulfaguanidine into the azanion results in very essential changes in the IR spectrum (Tables 2 and 3; Fig. 1). In agreement between theory and experiment, the conversion results in considerable frequency decreases in both ν^{as}(SO2) and $\nu^{as}(SO_2)$bands, which sum is: predicted 115 cm^{-1}, measured 110 cm^{-1}. The latter value is rationally larger than the corresponding values for other molecule-azanion pairs, containing additional electron-withdrawing groups (compound, SO_2 sum): o-sulfobenzimide (saccharin), 93 cm^{-1} [28]; o-sulfothiobenzimide (thiosaccharin), 60 cm^{-1} [30] and less than in sulfanilamide, 140 cm^{-1} [16].

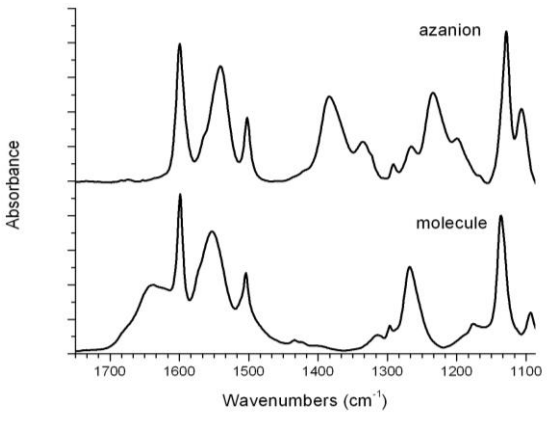


Fig. 1. Experimental IR spectra of sulfaguanidine and its azanion.

A new band was registered and it was attributed to the deformation δ(CNH^-) of deprotonated guanidine fragment. The band at 1600 cm^{-1} assigned as δ(NH_2) remained unchanged.

Table 2. Theoretical (B3LYP/6-311+G(2df,p)) and experimental (DMSO) IR data of sulfaguanidine molecule.

No.	B3LYP/6311+G(2df,p)			Approximate description [b]	Experimental data
	ν (cm^{-1})	ν[a] (cm^{-1})	A (km/mol)		
1	3687	3572	36.5	99 $\nu_{NH_2}^{as}$	3508 sh.
2	3676	3561	97.5	100 $\nu_{NH_2}^{as}$	3420
3	3676	3561	22.2	100 $\nu_{NH_2}^{as}$	- [c]
4	3576	3464	39.4	98 $\nu_{NH_2}^{s}$	3336
5	3576	3463	37.3	98 $\nu_{NH_2}^{s}$	- [c]
6	3496	3387	134.4	99 $\nu_{NH_2}^{s}$	3218
7	3199	3099	2.3	97 ν_{CH}	3088
8	3198	3098	1.5	96 ν_{CH}	3068
9	3160	3060	18.2	96 ν_{CH}	3056
10	3159	3060	12.3	97 ν_{CH}	3033
11	1679	1626	750.8	45 $\delta_{NH_2}^{guanidine}$, 26 $\nu_{N=C}$	1640
12	1659	1607	274.5	72 $\delta_{NH_2}^{amino}$	1600
13	1639	1587	90.8	32 ν_{CC}, 15 $\delta_{NH_2}^{amino}$	- [c]
14	1629	1578	230.8	68 $\delta_{NH_2}^{guanidine}$	1574
15	1613	1563	10.4	54 ν_{CC}, 13 δ_{CCC}	1554
16	1582	1533	238.8	49 $\delta_{NH_2}^{guanidine}$, 31 $\nu_{N=C}$	1509
17	1535	1487	55.9	61 δ_{CCH}	- [c]
18	1465	1419	66.8	32 ν_{CC}, 10 δ_{CCC}, 11 δ_{NCN}	1436
19	1462	1416	116.2	42 ν_{C-NH_2}, 10 δ_{NCN}	1420
20	1356	1314	3.9	40 ν_{CC}, 32 δ_{CCC}, 12 $\delta_{NH_2}^{amino}$	1316
21	1330	1289	70.4	54 δ_{CCH}, 31 ν_{CC}	1297
22	1313	1272	101.2	52 $\nu_{C-NH_2}^{amino}$	- [c]
23	1299	1258	201.1	92 $\nu_{SO_2}^{as}$	1269
24	1207	1169	4.0	68 δ_{CCH}	- [c]
25	1198	1160	115.6	46 $\delta_{NH_2}^{rock}$, 23 $\nu_{N=C}$, δ_{CCH}	1179
26	1151	1115	12.7	58 δ_{CCH}, 23 ν_{CC}, 10 $\delta_{NH_2}^{rock}$ (amino)	- [c]
27	1137	1101	213.6	39 $\nu_{SO_2}^{s}$, 22 ν_{CC}, 13 ν_{SC}	1137
28	1101	1063	23.2	48 δ_{CNH}, 23 ν_{C-NH_2}	1083
29[d]	1084	1047	88.1	25 $\nu_{SO_2}^{s}$, 18 δ_{CNH}	- [c]

[a] Scaled by 0.9858 [23].[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] These bands were not detected in the experimental spectrum. [d] Followed by 37 lower-frequency normal vibrations.

Table 3. Theoretical (B3LYP/6-311+G(2df,p) and experimental (DMSO) IR data of sulfaguanidine anion.

No.	B3LYP/6311+G(2df,p)			Approximate description [b]	Experimental data
	ν (cm^{-1})	ν[a] (cm^{-1})	A (km/mol)		
1	3636	3522	32.0	99 $\nu^{as}_{NH_2}$	-[c]
2	3632	3518	7.1	100 $\nu^{as}_{NH_2}$	-[c]
3	3540	3428	2.1	100 $\nu^{as}_{NH_2}$	-[c]
4	3502	3392	50.1	98 $\nu^{s}_{NH_2}$	-[c]
5	3490	3381	3.0	98 ν_{N^-H}	-[c]
6	3194	3094	5.0	97 ν_{CH}	-[c]
7	3180	3081	9.2	96 ν_{CH}	3030
8	3137	3039	31.6	96 ν_{CH}	-[c]
9	3134	3035	39.2	97 ν_{CH}	3080
10	1650	1598	93.9	67 $\delta^{amino}_{NH_2}$	1600
11	1636	1585	24.1	55 ν_{CC} , 15 $\delta^{amino}_{NH_2}$	-[c]
12	1621	1570	167.5	44 δ_{NH_2}, 19 ν_{C-N^-}	1564sh
13	1618	1567	12.6	45 ν_{CC} , 13 $\delta^{guanidine}_{NH_2}$	-[c]
14	1600	1550	654.8	48 ν_{C-N^-}, 28 $\delta^{guanidine}_{NH_2}$	1540
15	1530	1482	80.8	68 δ_{CCH}	1502
16	1453	1407	5.3	30 δ_{CCH} , 26 ν_{CC}	-[c]
17	1417	1373	273.5	33 δ_{C-N^-H} , 16 δ_{NH_2}	1384
18	1352	1309	1.1	53 δ_{CCH} , 22 ν_{CC}	1335
19	1324	1282	16.7	29 ν_{CC} , 20 δ_{CCH}	1291
20	1275	1235	65.2	48 $\nu^{amino}_{C-NH_2}$, 20 δ_{CCH}	1255
21	1241	1202	310.3	76 $\nu^{as}_{SO_2}$	1234
22	1219	1181	19.6	32 δ_{C-N^-H} , 16 ν_{C-NS}, 10 $\delta^{guanidine}_{NH_2}$	1199
23	1202	1164	12.8	82 δ_{CCH}	1166
24	1168	1131	192.9	51 $\delta^{guanidine}_{NH_2}$, 16 ν_{C-NS}	1128
25	1143	1108	8.5	60 δ_{CCH} , 17 $\delta^{rock}_{NH_2(amino)}$	-[c]
26[d]	1115	1080	162.0	42 $\nu^{s}_{SO_2}$, 26 ν_{CC}, 13 ν_{SC}	1106

[a] Scaled by 0.9858 [23].[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] These bands were not detected in the experimental spectrum. [d] Followed by 37 lower-frequency normal vibrations.

Structural analysis

According to both X-ray diffraction experimental data [6] and DFT calculations the sulfaguanidine molecule is composed of atoms lying approximately in two planes: one of the phenylene rings and amino group, and the other of the guanidine moiety. The angle between these planes has been experimentally found to be 94.4°; the same angle for the isolated sulfaguanidine molecule has been theoretically estimated at 96.7°. The corresponding value for the free sulfaguanidine anion is 82.1°.

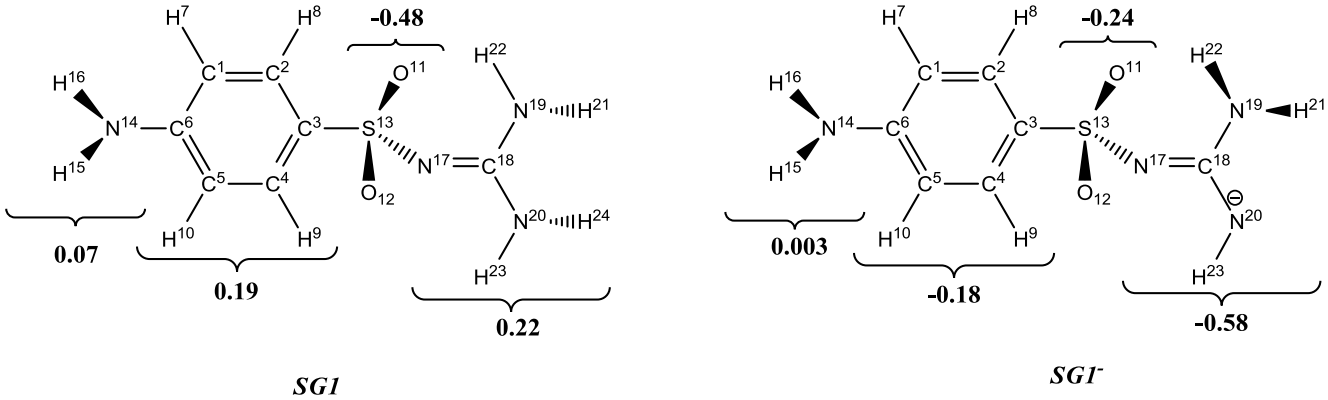
The theoretical and experimental bond lengths and angles in the sulfaguanidine and its azanion are listed in Table 4. As seen, there is a good agreement between the experimental and the theoretical values. The largest deviation from 0.053Å is in bond S_{13} - N_{17} and can be associated with the formation of hydrogen bonds in the solid state. The mean absolute deviations (m.a.d.) between theoretical and experimental bond lengths and angles of sulfaguanidine molecule are 0.017 Å and 1.06, respectively. This result leads us to believe that the theoretical bonds lengths and angle for the sulfaguanidine 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 [14,16,28,30]. They are strong shortening of the N_{20}-C_{18} and S_{13}-N_{17} bonds, strong lengthening of the C_{18}-N_{17} and C_{18}-N_{19} bonds.

The net electric charges q_i of the fragments of the species studied are given in Scheme 2. The charge change values $\Delta q_i = q_i$ (anion) - q_i (molecule)

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

	Molecule				Anion	
	Experimental [a]	Theoretical	Δ^b	Theoretical	∇^c	
Bond lengths [d]						
R(C^1C^2)	1.379	1.380	1.384	0.004	1.387	0.003
R(C^1C^6)	1.401	1.389	1.401	0.006	1.398	-0.003
R(C^2C^3)	1.387	1.387	1.391	0.004	1.393	0.002
R(C^3C^4)	1.388	1.388	1.392	0.004	1.389	-0.003
R(C^3S^{13})	1.767	1.763	1.773	0.008	1.814	0.041
R(C^4C^5)	1.378	1.386	1.383	0.001	1.391	0.008
R(C^5C^6)	1.379	1.380	1.402	0.023	1.395	-0.007
R(C^6N^{14})	1.399	1.396	1.386	-0.012	1.410	0.024
R($O^{11}S^{13}$)	1.445	1.450	1.466	0.019	1.476	0.010
R($O^{12}S^{13}$)	1.442	1.430	1.446	0.010	1.458	0.012
R($N^{17}S^{13}$)	4.589	1.587	1.642	0.053	1.576	-0.066
R($N^{17}C^{18}$)	1.343	1.340	1.302	-0.039	1.374	0.072
R($C^{18}N^{19}$)	1.336	1.326	1.356	0.025	1.401	0.045
R($C^{18}N^{20}$)	1.322	1.337	1.372	0.043	1.296	-0.076
Bond angles [d]						
A($C^2C^1C^6$)	121.0	120.5	120.6	-0.150	120.7	0.100
A($C^1C^2C^3$)	120.1	120.0	120.0	-0.050	120.4	0.400
A($C^2C^3C^4$)	119.6	119.8	120.1	0.400	119.1	-1.000
A($C^2C^3S^{13}$)	121.8	121.2	120.3	-1.200	120.5	0.200
A($C^4C^3S^{13}$)	118.5	119.0	119.7	0.950	120.3	0.600
A($C^3C^4C^5$)	120.4	119.9	120.0	-0150	120.6	0.600
A($C^4C^5C^6$)	120.5	120.8	120.7	0.050	120.6	-0.100
A($C^1C^6C^5$)	118.3	119.0	118.7	0.050	118.6	-0.100
A($C^1C^6N^{14}$)	120.4	121.2	120.7	-0.100	120.6	-0.100
A($C^5C^6N^{14}$)	121.2	119.8	120.6	0.100	120.8	0.200
A($C^3S^{13}O^{11}$)	107.0	107.2	107.5	0.400	104.7	-2.800
A($C^3S^{13}O^{12}$)	107.7	107.9	108.1	0.300	104.5	-3.600
A($C^3S^{13}N^{17}$)	106.0	106.1	101.9	-4.150	106.7	4.800
A($O^{11}S^{13}O^{12}$)	115.0	116.5	118.0	2.250	115.6	-2.400
A($O^{11}S^{13}N^{17}$)	114.3	112.6	111.9	-1.550	115.2	3.300
A($O^{12}S^{13}N^{17}$)	106.2	105.9	108.3	2.250	109.2	0.900
A($S^{13}N^{17}C^{18}$)	121.5	121.6	123.6	2.050	126.1	2.500
A($N^{17}C^{18}N^{19}$)	124.7	126.5	127.4	1.800	120.3	-7.100
A($N^{17}C^{18}N^{20}$)	116.5	116.2	117.1	0.750	122.8	5.700

[a]See Ref. [8]. [b]Algebraic deviations (Å, degrees) between theoretical and experimental values. [c] Algebraic deviations (Å, degrees) between theoretical values of the anion and molecule. [d] Atom numbering according to Scheme 1.



Scheme 2. Mulliken net electric charges q_i over fragments of sulfaguanidine molecule **SG1** and its azanion **SG1**$^-$.

are usually quite informative in showing the distributions of the new charges in anions (Refs. [28-30] and references therein). According to the present calculations, the anionic charge of azanion is distributed, as follows: -0.07 e^-, -0.37 e^- and -0.56 e^- are delocalized over the amino group, phenylene ring and sulfonylguanidine fragment, respectively.

CONCLUSION

The spectral and structural changes, caused by the conversion of the sulfaguanidine 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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REFERENCES

1. R. O. Roblin Jr., J. H. Williams, Ph. S. Winnek, J. P. English, *J. Am. Chem. Soc.*, **62**, 2002 (1940).
2. E. K. Marshall, A. C. Bratton, H. J. White, J. T. Litchfield, *Johns Hopkins Hosp. Bull.*, **67**, 163 (1940).
3. M. Kuhnert-Brandstätter, *Oesterr. Apoth. Ztg.*, **13**, 297 (1959).
4. M. Kuhnert-Brandstätter, S. Wunsch, *Microchim. Acta*, 1297 (1969).
5. S. S. Yang, J. K. Guillory, *J. Pharm. Sci.*, **61** (1972) 26.
6. C. H. Koo, H. S. Kim, W. Shin, C. Choe, *J. Kor. Chem. Soc.*, **18**, 97 (1974).
7. M. Alleaume, *Acta Cryst.*, **B32**, 669 (1976).
8. A. Kalman, M. Czugler, G. Argay, *Acta Cryst.*, **B37**, 868 (1981).
9. G. Schwenker, *Arch Pharm.* **295**, 753 (1962).
10. M. Brandstätter, F. Bachleitner-Hofmann, *Spectrohim. Acta*, **A27**, 191 (1971).
11. N. V. Trius, *Khim.-Farm. Zh.*, **13**, 103 (1979).
12. A. Chandran, H. T. Varghese, C. Yohannan, G. Rajendran, *Orient. J. Chem.*, **27**, 611 (2011).
13. G. R. Sullivan, J. D. Roberts, *J. Org. Chem.*, **42**, 1095 (1977).
14. A. D. Popova, E. A. Velcheva, B. A. Stamboliyska, *J. Mol. Struct.*, **1009**, 23 (2012).
15. E. A. Velcheva, B. A. Stamboliyska, P. J. Boyadjiea, *J. Mol. Struct.*, **963**, 57 (2010).
16. A. D. Popova, M. K. Georgieva, O. I. Petrov, K.V. Petrova, E. A. Velcheva, *Int. J. Quant. Chem.*, **107**, 1752 (2007).
17. S. Stoyanov, J. A. Tsenov, D. Y. Yancheva, *J. Mol. Struct.*, **1009**, 42 (2012).
18. S. Stoyanov, *J. Phys. Chem.*, **114** 5149 (2010).
19. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J.Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P.

Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A1, Gaussian Inc., Wallingford CT, 2009.
20. A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
21. C. Lee, W. Yang, G. R. Parr, *Phys. Rev*., **B37**, 785 (1998).
22. H. J. Michal, VEDA 4, Warsaw, 2004.
23. J. P. Merrick, D. Moran, L. Radom, *J. Phys. Chem*., **A111**, 11683 (2007).
24. I. Minkin, B. Y. Simkin, R. M. Minyaev, Quantum chemistry of organic compounds. Mechanisms of reactions, Springer, Heidelberg, 1990.
25. B. E. Ballard, E. Nelson, *J. Pharmacol. Exp. Ther*., **135**, 120 (1962).
26. B. C. Rudy, B. Z. Senkowski, *Analyt Profiles*., **2**, 234 (1973).
27. I. G. Binev, B. A. Stamboliyska, E. A. Velcheva, *Spectrochim. Acta Part A*, **52**, 1135 (1996).
28. J. A. Tsenov, S. S. Stoyanov, I. G. Binev, *Bulg. Chem. Commun.*, **40**, 538 (2008).
29. J. A. Tsenov, S. S. Stoyanov, I. G. Binev, *Bulg. Chem. Commun.*, **37**, 361 (2005).
30. Y. G. Binev, C. T. Petkov, L. Pejov, *Spectrochim. Acta*, **A56**, 1949 (2000).

ЕКСПЕРИМЕНТАЛНО И ТЕОРЕТИЧНО ИЗСЛЕДВАНЕ НА ИЧ СПЕКТРАЛНИ И СТРУКТУРНИ ПРОМЕНИ, ПРОИЗТИЧАЩИ ОТ ПРЕВРЪЩАНЕТО НА 4-АМИНО-N-[АМИНО(ИМИНО)МЕТИЛ] БЕНЗЕНСУЛФОНАМИД (СУЛФАГУАНИДИН) В АЗАНИОН

А. Попова*, Б. Стамболийска, Е. Велчева

Институт по Органична химия с Център по Фитохимия, Българска Академия на Науките, ул. Акад. Г. Бончев, бл. 9, 1113 София, България

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(Резюме)

Структурата на амино-N-[амино(имино)метил]бензенсулфонамид (сулфагуанидин) и неговия азанион са изследвани с помощта на инфрачервени спектри и DFT пресмятания. Намерено е добро съответствие между експерименталните и теоретичните вибрационни характеристики на изследваните частици. Използваният теоретичен метод добре предсказва силните спектрални промени, възникващи при превръщането на молекулата на сулфагуанидина в азанион. Превръщането в азанион поражда и значителни промени в структурата *при* и *непосредствено до* азанионния център. Според изчисленията новият (азанионен) заряд е разпределен както следва: -0.07 e^-, -0.37 e^- и -0.56 e^- върху амино групата, фениленовото ядро и сулфонилгуанидиновия фрагмент, съответно.