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IR Spectral and Structural Studies of 4-Aminobenzenesulfonamide (Sulfanilamide)-d_0, -d_4, and -^{15}N, As Well As Their Azanions: Combined DFT B3LYP/Experimental Approach

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ABSTRACT: The infrared (IR) spectra of sulfanilamide **1** and of its azanion (counter ion Na$^+$) **2** have been measured in dimethyl sulfoxide (DMSO) solutions. The density functional theory (DFT) B3LYP 6-31++G(d,p) computations performed adequately describe the experimental spectroscopic data, including the corresponding frequency isotopic shifts. In agreement between theory and experiment, the conversion of sulfanilamide **1** into azanion **2** results in strong frequency decreases of the asymmetrical and symmetrical vibrations of the SO$_2$ group: predicted 122 cm^{-1}, measured 140 cm^{-1} in solution (total values), as well as in other essential IR spectral changes. According to the computations, the strongest changes in the steric structure take place at and next to the azanionic center. The new (azanionic) charge is distributed, as follows: 0.08e$^-$, 0.23e$^-$, and 0.12e$^-$ are delocalized over the amino, phenylene, and sulfonic groups, respectively, and 0.57e$^-$ of it remain localized at the azanionic center. © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 107: 1752–1764, 2007

Key words: IR; B3LYP; 4-aminobenzensulfonamide (sulfanilamide); anion; structure; isotope labeling

Introduction

Gelmo [1] was the first to prepare sulfanilamide (formula **1**) almost 100 years ago. This compound was the simplest representative of a large series of sulfonamide medicines. Their strong antibacterial activity combined with low toxicity was discovered by Domagk in 1934 (Nobel Prize 1939) [2]. Under trade names such as Prontosil album, and Streptocide album, sulfanilamide is used against various bacterial infections in human and veterinary medical practices [3, 4].

The early work on infrared (IR) spectra of sulfanilamide was reviewed by Bellamy [5], together with the main band assignments. A detailed empirical assignment of IR and Raman bands of sulfanilamide was reported 40 years ago [6]. The complete IR band assignment of the sulfanilamide molecule was recently performed using ab initio Hartree–Fock (HF) 3-21G force-field calculations [7]:
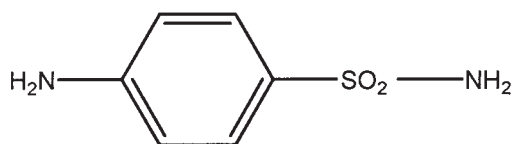
1
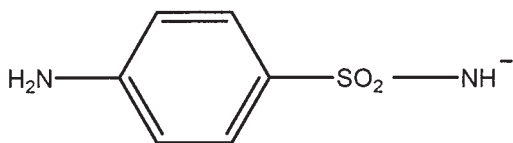
2

In contrast, 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, 9]. The molecule → anion conversions for many species have recently been studied successfully by ab initio and/or density functional theory (DFT) and IR spectra (Refs. [10–14] and references therein). The title compound is an interesting and convenient object of such investigations, as it contains several characteristic groups (e.g., SO_2, NH_2) and can easily be converted into a stable azanion. Neither the IR spectra nor structure

of sulfanilamide azanion (formula 2) 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 sulfanilamide molecule **1** into the corresponding azanion **2** on the basis of both DFT B3LYP 6-31(d,p) computations and spectroscopic experiments.

Computations

DFT computations (full optimization) of the title species were performed using the Gaussian 98 program package [15]. This theory was the groundwork of series of cost-effective methods to approximate electron correlation effects [16]. We employed the B3LYP functional, which combines Becke's three-parameter nonlocal exchange with the correlation functional of Lee, Yang, and Parr [17, 18], adopting a 6-31++G(d,p) basis set without any symmetry restriction. For every structure, the stationary points found on the molecular potential energy hypersurfaces (PEHS) were characterized using standard analytical harmonic vibrational analysis. The absence of negative frequencies or negative eigenvalues of the second-derivative matrix confirmed that the stationary points correspond to global minima on the PEHS [16]. The use of 6-31++G(d,p) basis set in DFT computations has recently resulted in better or equally good spectral and structural predictions, compared with other basis sets for both organic molecules and anions [11, 12, 19, 20]. No scaling in the density functional force field was done. A standard least-squares program was used to calculate the single-parameter linear regression indices.

Experimental

We prepared sulfanilamide-d_0 by the classical Gelmo method [1] from acetanilide (Scheme 1). After recrystallization, we obtained white needles of **1**, m.p. 165–166°C (literature m.p. 164.5–166.5°C) [3].

To prepare sulfanilamide-^{15}N (in the sulfonamido group), we used $^{15}NH_3$ (Isocommezz, 97.3% at. enrichment) for the second reaction of Scheme 1. We prepared sulfanilamide-d_4 (in amino groups) by threefold, dissolving **1** in D_2O (Fluka, 99.8% at. enrichment) and evaporation of the solvent in vacuo. The sulfanilamide azanion **2** (counter ion Na^+) and its isotope-labeled derivatives were pre-
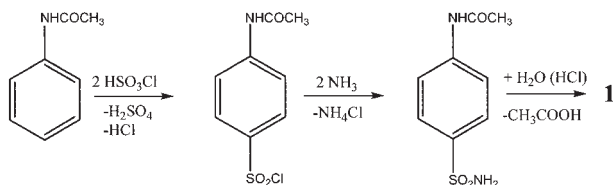
SCHEME 1. Preparation of sulfanilamide **1** by Gelmo's method.

pared by adding dimethyl sulfoxide (DMSO)-d_6 solutions of sulfanilamide-d_0, -d_4, and -^{15}N to excess of NaOCH$_3$-d_0 and -d_3, and filtration of the reaction mixture by a syringe filter. The conversion was practically complete: no bands of **1** were seen in the spectra after metalation.

IR spectra were measured on a Brucker IFS 113v Fourier transform infrared (FTIR) spectrophotometer in a CaF$_2$ cell of 0.13 mm (for 0.20 mol l^{-1} DMSO-d_6 solutions), a KBr cell of 0.6 mm (for saturated CDCl$_3$ solutions), KBr and CsI disks, at a resolution of 1 cm^{-1} and 50 scans.

Results and Discussion

ENERGY ANALYSIS

We calculated the total energies of the most stable conformers of **1** and **2**, as well as that of the tautomeric anion **3** (obtained hypothetically if the metalation had taken place at the phenylamino group) (Fig. 1). Table I shows that the calculated energy difference of the molecular conformers is 4.13 kJ mol^{-1} and that of the anionic conformers is smaller, 0.87 kJ mol^{-1}. The energy difference between the most stable anionic and molecular conformers $E^D = E$ (anion) $- E$ (molecule) is a measure of the Broensted acidity of a given compound in the gas phase [21]. Georgieva and Velcheva [12] recently found that B3LYP++G(d,p) E^D values of a series of C—H, N—H and O—H acids correlate fairly well (correlation coefficient $R = 0.94$) with the corresponding pK_a, measured in DMSO. Having in mind $E^D = 1444.75$ kJ mol^{-1} (Table I) and the correlation equation pK_a (DMSO) $= 0.11507$. $E^D -$ 150.04 (kJ mol^{-1}) [12], we estimated a 'theoretical' pK_a (DMSO) of sulfanilamide at 16.2. There are no literature data for pK_a (DMSO), but we can suppose that sulfanilamide is a moderately weak N—H acid in DMSO. Deprotonation of sulfanilamide with the formation of **3** is less probable (Table I).

CORRELATION ANALYSIS

Comparison of the native B3LYP 6-31++G(d,p) vibrational frequencies of sulfanilamide **1a** with those we have measured under various conditions (see the next section, Spectral Analysis) resulted in the formation of excellent correlations ($0.99 > R > 1$; Table II). We shall use them for correlational scalings of theoretical frequencies. According to Alcolea's review article [22], the use of correlation equations instead of scaling coefficients leads to better results, especially for the low-frequency vibrations.

SPECTRAL ANALYSIS

Sulfanilamide-d_0

The numerical characteristics of the theoretical and experimental spectra of sulfanilamide **1a** are compared in Table III. Let us consider the solid-state spectrum in the v_{NH_2} region (Fig. 2, Table III).

With respect to both the method of isolation (experimental) and the IR spectra, our sample corresponds to polymorph I of sulfanilamide [23]. The authors assigned the bands (in the frequency decrease order in the solid-state IR spectrum), as follows: $\delta_{NH_2}^{as}$ (amino), $\delta_{NH_2}^{s}$ (amino), $\delta_{NH_2}^{as}$ (amido), and $\delta_{NH_2}^{s}$ (amido) [23].

However, a new assignment has recently appeared [7] (in the same order): $\delta_{NH_2}^{as}$ (amino), $\delta_{NH_2}^{as}$ (amido), $\delta_{NH_2}^{s}$ (amino), and $\delta_{NH_2}^{s}$ (amido) [7]. We prove the first assignment [23] as follows:

1. Bands at 3462 and 3374 cm^{-1} (solid state, Table III) are not present in the solid-state IR spectrum of benzenesulfonamide C$_6$H$_5$SO$_2$NH$_2$, and the other two bands appear at almost the same places [24].

2. The solubility of sulfanilamide in chloroform is very low; nevertheless, we succeeded in measuring spectra in CDCl$_3$. All v_{NH_2} frequencies of the spectra in CDCl$_3$ were higher than those in the solid state, due to the strong hydrogen bond destruction. However, amido groups form much stronger hydrogen bonds than are formed by amino groups. This difference resulted in rearrangement of the v_{NH_2} frequencies, and the new order (solvent CDCl$_3$) corresponded to the theoretical one (Table III).

3. The substitution of ^{14}N of the sulfonamide group by ^{15}N resulted in frequency decreases
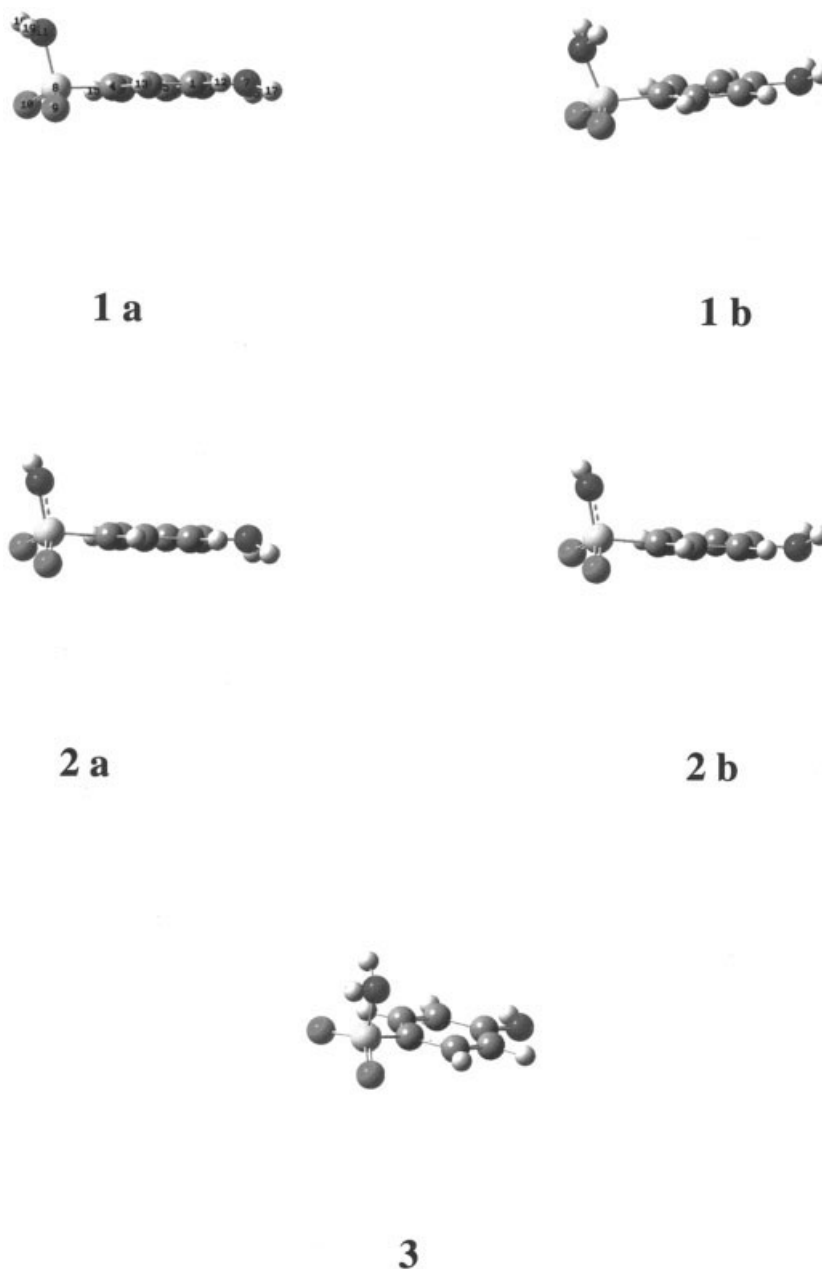
FIGURE 1. Stable conformers of sulfanilamide (**1a**, **1b**), its anion (**2a**, **2b**) and of the hypothetic anionic tautomer $^-NH-C_6H_5-SO_2-NH_2$ (**3**).

of the band at 3343 cm^{-1} by 11 cm^{-1} and that at 3247 cm^{-1} by 7 cm^{-1} (solid state); the bands at 3462 cm^{-1} and 3374 cm^{-1} remained at the same places.

Introducing ^{15}N instead of ^{14}N in the sulfonamide group led to the following additional IR changes:

1. Vibration 28 (Table III), dominated by the υ_{S-N} coordinate, underwent a 14 cm^{-1} frequency decrease.
2. The computations predicted very close frequencies of vibrations *33* and *34* of the unlabeled sulfanilamide, so we ascribed the band at 703 cm^{-1} as a superposition of the corresponding bands (Table III). Two new bands,

Total energies E (in hartree) and differences between them ΔE (in kJ mol^{-1}) of the species studied.

No.	Species	E (native)	E (corrected)[a]	$\Delta E^{a,b}$
1	Sulfanilamide **1a**	−891.572889	−891.429390	0
2	Sulfanilamide **1b**	−891.571630	−891.427817	4.1299
3	Sulfanilamide anion **2a**	−891.008642	−890.879113	1444.7523
4	Sulfanilamide anion **2b**	−891.008629	−890.878783	1445.6187
5	Sulfanilamide anion **3**	−891.006113	−890.876397	1451.88

[a] With corrections for zero-point vibrational energy (ZPVE).
[b] $\Delta E = E_n - E_1$.

at 708 cm^{-1} and 697 cm^{-1}, with opposite isotopic shifts (+5 and −6 cm^{-1}) appeared in the spectrum of sulfanilamide-^{15}N instead of the cited above band superposition.

3. These results can be considered as proof for the assignments of the bands mentioned. We shall also discuss the IR spectrum of sulfanilamide-d_0 with the relation to both deuteration and conversion into azanion in the next subsections.

Sulfanilamide-d_4

The solid-state IR spectrum of this compound is compared with the spectrum of the nonlabeled species in Figure 2. We can see the high deuteration level of our sample. The numerical theoretical and experimental IR characteristics of sulfanilamide-d_4 (labeled in the amino groups) are listed in Table IV.

It is also seen in Table IV and Figure 3 that the deuteration has led to very essential IR changes affecting mainly vibrations with decisive participations of the two NH$_2$ groups. The large negative

isotope shifts correspond to $\nu^{as}_{NH_2}$, $\nu^s_{NH_2}$, and $\delta^{sc}_{NH_2}$ vibrations of both amino and amido groups. As should be expected on the basis of the computations (Table IV), the isotope shifts of the remaining IR bands are not essential.

The $\Delta\Delta\nu$ value (the last column of Table IV) is a quantitative measure of the agreement between theoretical and experimental isotope shifts. Their sum is 288 cm^{-1}, the sum of the absolute values of the experimental isotope shifts $\Sigma/\Delta\nu_{exp}/$ is 4197 cm^{-1}, and the ratio of the sums is 0.069 or 6.9%. The latter result should be considered a very good one, as the frequency shifts are more sensitive, hence more informative than the frequencies themselves for estimating the accuracy of the computations [25]. For example, the corresponding ratio value in the case of nicotinamide-d_0 and -d_2 was found to be essentially large (i.e., worse), 18.3% [25].

Sulfanilamide Azanion-d_0

Organic anions are not soluble in common spectroscopic solvents and usually react with them. So,

Correlations between calculated and measured IR frequencies of sulfanilamide, according to the equation $\nu_{exp} = \rho\nu_{theor} + b$ (cm^{-1}).

No.	Experimental conditions	ρ^a	b^b	R^c	SD^d	n^e
1	Solution in CDCl$_3$	0.93957	61.98	0.99960	31.9	13
2	Solution in DMSO-d_6	0.90785	109.7	0.99695	16.3	10
3	Solid in KBr/CsI	0.91940	65.9	0.99950	31.5	30

[a] Slope.
[b] Intercept.
[c] Correlation coefficient.
[d] Standard deviation.
[e] Number of data points.

TABLE III

Theoretical [B3LYP 6-31++G(d,p)] and experimental (CDCl$_3$ solution and solid-state) IR frequencies (ν in cm^{-1}) and integrated (A in km mol^{-1}) or relative intensities of sulfanilamide-d$_0$.

No.	B3LYP6-31++G(d,p)			Experimental data[a]	
	ν[b]	A	Approximate description[c]	in CDCl$_3$ ν	in KBr ν
1	3471	24.5	$\nu_{NH_2}^{as}$ (amino)	3500 w	3462 s
2	3401	42.9	$\nu_{NH_2}^{as}$ (amido)	3471 w	3343 s
3	3368	44.0	$\nu_{NH_2}^{s}$ (amino)	3439 w	3374 vs
4	3293	36.7	$\nu_{NH_2}^{s}$ (amido)	3414 m	3247 s
5	3027	2.3	ν_{PhH}	—[d]	—[d]
6	3025	1.5	ν_{PhH}	—[d]	—[d]
7	2992	15.7	ν_{PhH}	—[d]	—[d]
8	2991	11.7	ν_{PhH}	—[d]	—[d]
9	1601	233.9	$\delta_{NH_2}^{sc}$ (amino), $\nu_{CC(Ph)}$	1623 m	1638 s
10	1608	69.5	$\nu_{CC(Ph)}$, δ_{PhH}, $\delta_{NH_2}^{sc}$ (amino)	1597 m	1600 s
11	1556	10.1	$\nu_{CC(Ph)}$, $\delta_{CC(Ph)}$	—[d]	1573 w
12	1525	26.1	$\delta_{NH_2}^{sc}$ (amido)	—[d]	1549 w
13	1479	56.5	δ_{PhH}, $\nu_{CC(Ph)}$, ν_{C-N}	1505 w	1505 m
14	1416	6.1	δ_{PhH}, $\nu_{CC(Ph)}$, $\delta_{NH_2}^{rock}$ (amino)	1381 m	1438 w
15	1329	12.0	$\nu_{CC(Ph)}$, δ_{PhH}, $\delta_{NH_2}^{rock}$ (amino), $\nu_{SO_2}^{as}$	1346 m	1336 w
16	1291	4.9	δ_{PhH}, $\nu_{CC(Ph)}$	—[d]	—[d]
17	1282	91.9	ν_{C-N}, $\nu_{CC(Ph)}$, δ_{PhH}, ν_{C-S}	—[d]	—[d]
18	1269	187.8	$\nu_{SO_2}^{as}$, $\delta_{NH_2}^{rock}$ (amido), $\nu_{CC(Ph)}$	1322 m	1312 vs
19	1177	12.2	δ_{PhH}, ν_{C-S}, δ_{CCC}	1187 w	1188 w
20	1126	12.2	$\delta_{NH_2}^{rock}$ (amino), δ_{PhH}, $\nu_{CC(Ph)}$	—[d]	—[d]
21	1104	270.9	$\nu_{SO_2}^{s}$, δ_{CCC}, ν_{C-S}	1160 s	1146 vs
22	1066	13.0	δ_{CCC}, $\delta_{NH_2}^{rock}$ (amido)	1099 w	1097 s
23	1058	72.1	$\nu_{SO_2}^{s}$, $\gamma_{NH_2}^{tw}$ (amino), $\gamma_{NH_2}^{tw}$ (amido), δ_{CCC}	—[d]	—[d]
24	1052	2.5	$\delta_{NH_2}^{rock}$ (amino), δ_{CCC}, $\delta_{NH_2}^{rock}$ (amido)	—[d]	—[d]
25	1004	4.9	δ_{CCC}, $\nu_{SO_2}^{s}$, ν_{C-S}	—[d]	1003 w
26	963	0.2	γ_{PhH}	—[d]	—[d]
27	950	0.1	γ_{PhH}	—[d]	—[d]
28	854	163.2	ν_{N-S}, δ_{CCC}, ν_{C-S}, $\gamma_{NH_2}^{wag}$ (amido)	—[d]	899 m
29	837	46.3	ν_{N-S}, γ_{PhH}, $\gamma_{NH_2}^{wag}$ (amido)	—[d]	826 s
30	827	38.2	δ_{CCC}, $\gamma_{NH_2}^{wag}$ (amido), ν_{C-S}, γ_{PhH}	—[d]	—[d]
31	822	0.5	γ_{PhH}	—[d]	—[d]
32	731	6.2	γ_{PhH}, τ_{CCCC}	—[d]	—[d]
33	669	131.3	$\gamma_{NH_2}^{wag}$ (amido), δ_{CCC}, ν_{C-S}	—[d]	703 m
34	668	133.6	ν_{S-N}, δ_{CCC}, ν_{C-S}	—[d]	703 m
35	661	3.0	$\delta_{CCC(Ph)}$	—[d]	—[d]
36	561	68.5	τ_{CCCC}, $\delta_{O=S-C}$	—[d]	565 m
37	554	32.9	γ_{PhH}, $\gamma_{NH_2}^{wag}$ (amino), δ_{NSC}, $\delta_{SO_2}^{sc}$	—[d]	539 m
38	504	53.3	δ_{NSC}, $\delta_{SO_2}^{sc}$, γ_{PhH}, $\gamma_{NH_2}^{wag}$ (amino)	—[d]	—[d]
39	481	274.8	$\delta_{NH_2}^{wag}$ (amino), δ_{CCC}	—[d]	455 w
40	477	67.4	$\gamma_{NH_2}^{wag}$ (amino), δ_{CCC}	—[d]	—[d]
41	452	0.1	τ_{CCCC}	—[d]	—[d]
42	419	0.4	δ_{CCC}, $\delta_{O=S-C}$, δ_{CCN}	—[d]	390 m[e]
43	392	10.7	τ_{CCCC}, δ_{C-S-N}, $\delta_{SO_2}^{sc}$	—[d]	350 m[e]
44	382	8.1	$\gamma_{SO_2}^{tw}$, δ_{CCC}	—[d]	341 s[e]
45	372	8.2	δ_{CCC}, δ_{CCN}	—[d]	—[d]
46	326	1.2	δ_{CCC}, ν_{C-S}	—[d]	297 m[e]
47	257	2.3	τ_{CCCC}, δ_{CSN}	—[d]	226 m[e]
48	218	0.8	δ_{CCC}, $\delta_{SO_2}^{wag}$	—[d]	179 w[e]
49	173	31.0	$\gamma_{NH_2}^{tw}$ (amido), τ_{sk}	—[d]	147 s[e]
50	145	5.7	τ_{sk}	—	—
51	90	0.5	τ_{sk}	—	—

[a] Relative intensities: s, strong; m, moderate; w, weak; v, very.
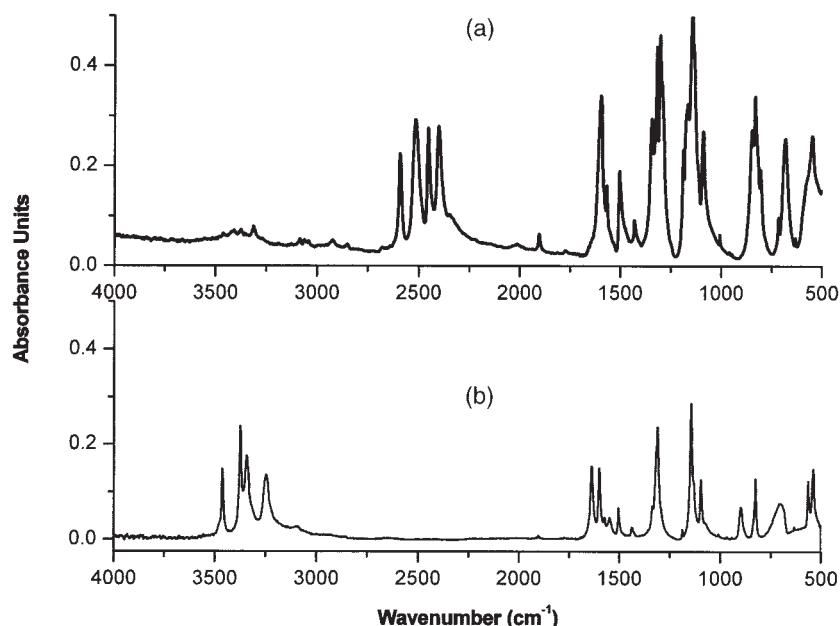
[b] Scaled, according to correlation equation No. 3 (Table II).

[c] Vibrational modes: ν, stretching; δ, in-plane bending; γ, out-of-plane bending; τ, torsion. Superscripts: s, symmetrical; as, asymmetrical; sc, scissoring; rock, rocking; wag, wagging; tw, twisting. Subscript: sk, skeletal.

[d] No reliable data.

[e] In a CsI disk for the far IR region.

FIGURE 2. IR spectra (solid, in KBr) of sulfanilamide-d_0 (b) and sulfanilamide-d_4 (a).

polar aprotonic solvents, most frequently DMSO, are used to study the IR spectra of organic anionic derivatives (Refs. [8–12, 14, 19, 20, 26] and references therein). Sulfanilamide azanion (e.g., sulfanilamide itself) is highly soluble and very stable in DMSO. To perform a correct comparison of the IR spectra of sulfanilamide-d_0 and -d_4 with those of their azanions, we shall consider their DMSO solution spectra (Tables V–VIII and Fig. 3). As in the preceding subsection, we shall now use theoretical data for the most stable conformers **1a** and **2a** of the species studied (Table I, Fig. 1).

The frequencies of the very strong $v^{as}_{SO_2}$ and $v^{s}_{SO_2}$ bands measured in DMSO (Table V) agree well with those measured in the solid state (cf. Table III). The theoretical method used predicts these frequencies fairly well: the sum of their B3LYP 6-31++G(*d,p*) values is only 32 cm^{-1} (native) or 37 cm^{-1} (scaled) less than the sum of the frequencies measured experimentally. For comparison, the corresponding deviation, found by the authors [7] at the ab initio HF 3-21G level, was −519 cm^{-1} (native). The same investigators obtained a much larger deviation, −865 cm^{-1} (native) on the basis of PM3 calculations [27].

By analogy with the cases of sulfanilamide-d_0 and -d_4 in the solid state, we compared the IR spectra of same species in DMSO-d_6 solutions (Table VI). We calculated a value $\Sigma\Delta\Delta v_i / \Sigma / v_{i(exp)}$ of

17.4% in the present case or 2.5-fold larger (i.e., worse) than that found in the preceding subsection.

Now we can compare data in Tables V and VII and in VI and VIII; these comparisons will make it possible to discuss the IR changes, caused by the conversion of sulfanilamide-d_0 and -d_4 into the corresponding azanions -d_0 and -d_3.

We can see in Tables V and VII and Figure 3 that the conversion produces essential IR spectral changes:

1. Both $v^{as}_{SO_2}$ and $v^{s}_{SO_2}$ bands undergo essential frequency decreases, which sum is: predicted 122 cm^{-1}, measured 140 cm^{-1}. The latter value is rationally lower than the corresponding decreases found in other cases of molecule → azanion pairs, containing additional electron-withdrawing groups (compound, Δv_{SO_2} sum): *o*-sulfobenzimide (saccharin), 93 cm^{-1} [28]; *o*-sulfothiobenzimide (thiosaccharin), 60 cm^{-1} [29].

2. The **1a** → **2a** conversion studied leads to a 1.6-fold increase in the sum of the integrated intensities of the phenylene bands $8_{a,b}$ and $19_{a,b}$ (Wilson's notation). This result is in agreement with the intensity increases of those bands in cases of many other anionic substituents [30].

TABLE IV

Theoretical [B3LYP 6-31++G(d,p)] and experimental (solid, in KBr) IR frequencies (v, in cm^{-1}) and integrated (A in km mol^{-1}) or relative intensities of sulfanilamide-d$_4$, and the corresponding isotope shifts.

No.	B3LYP 6-31++G(d,p)			Experimental and other data			
	v^a	A	Approximate description^b	v^c	Δv^d_{theor}	Δv^d_{theor}	$\Delta\Delta v^f$
1	3027	2.5	v_{PhH}	3085 w	0	—^{g}	—
2	3025	0.9	v_{PhH}	3085 w	0	—^{g}	—
3	2992	15.3	v_{PhH}	3061 w	0	—^{g}	—
4	2991	14.1	v_{PhH}	3035 w	−1	—^{g}	—
5	2584	12.8	v^{as}_{N-D} (amino)	2592 m	−917	−870	47
6	2529	27.3	v^{as}_{N-D} (amido)	2516 s	−901	−827	74
7	2453	46.1	v^{s}_{N-D} (amino)	2454 s	−946	−920	26
8	2395	30.5	v^{s}_{N-D} (amido)	2403 s	−928	−844	84
9	1583	212.5	δ_{PhH}, v_{CC}	1599 s	4	−1	5
10	1553	9.3	δ_{PhH}, v_{CC}	1567 w	−4	−6	22
11	1480	76.6	δ_{PhH}, v_{C-N}, v_{CC}	1504 m	1	−1	0
12	1408	4.4	δ_{PhH}, v_{CC}	1431 w	−8	−6	2
13	1320	154.9	$\delta^{sc}_{ND_2}$ (amino), δ_{PhH}, v_{CC}	1320 v	−291	−318	27
14	1312	17.7	v_{CC}, $\delta^{sc}_{ND_2}$ (amino)	—	—^{h}	—	—
15	1290	0.3	δ_{PhH}	—	−1	—	—
16	1260	194.9	$v^{as}_{SO_2}$, δ_{PhH}	1304 v	−10	−8	2
17	1178	11.4	δ_{PhH}, $\delta^{sc}_{ND_2}$ (amino)	1190 w	−2	2	0
18	1154	39.9	$\delta^{sc}_{ND_2}$ (amido), δ_{PhH}, $\delta^{sc}_{ND_2}$ (amino)	1168 s	−384	−381	3
19	1148	12.6	$\delta^{sc}_{ND_2}$ (amido), $\delta^{sc}_{ND_2}$ (amino), δ_{PhH}	—	—	—	—
20	1119	14	δ_{PhH}	—	—	—	—
21	1098	255.0	$v^{s}_{SO_2}$, v_{C-S}, $\delta^{sc}_{ND_2}$ (amido), δ_{CCC}	1145 v	−6	−1	5
22	1055	79	δ_{CCC}, $v^{s}_{SO_2}$, $\delta^{sc}_{ND_2}$ (amido)	1090 m	−12	−7	5
23	1003	4.6	δ_{CCC}	1008 w	−1	5	6
24	963	0.1	γ_{PhH}	—	0	—	—
25	950	0.02	γ_{PhH}	—	0	—	—
26	855	0.3	δ_{CCC}, $\gamma^{wag}_{ND_2}$ (amino)	—	1	—	—
27	839	50.3	γ_{PhH}, $\gamma^{tw}_{ND_2}$ (amido)	847 m	—	—	—
28	834	21.6	γ_{PhH}, $\gamma^{tw}_{ND_2}$ (amido)	833 s	—	—	—
29	826	34.6	δ_{CCC}, v_{C-N}, γ_{PhH}, $\gamma^{tw}_{ND_2}$ (amido)	805 w	−2	—	—
30	821	0.5	γ_{PhH}	—	−2	—	—
31	775	207.5	v_{N-S}, v_{PhS}	683 s	—^{h}	—	—
32	729	8.2	γ_{PhH}, τ_{CCCC}	—	—^{h}	—	—
33	660	3.7	δ_{CCC}	633 w	−1	—	—
34	657	23.4	δ_{CCC}, $\gamma^{tw}_{SO_2}$, v_{N-S}	580 m	—^{h}	—	—
35	595	110.3	$\gamma^{wag}_{ND_2}$ (amido), δ_{CCC}	548 m	—^{h}	—	—
36	558	27.7	γ_{PhH}	500 w	—^{h}	—	—
37	513	83.4	$\gamma^{wag}_{ND_2}$ (amido)	454 w	—^{h}	—	—
38	497	8.2	$\delta^{sc}_{SO_2}$, $\gamma^{wag}_{ND_2}$ (amido), τ_{CCCC}	—	—	—	—
39	460	2.2	$\gamma^{tw}_{ND_2}$ (amido)	418 w	—^{h}	—	—
40	452	0.1	τ_{CCCC}	—	—	—	—
41	401	128.3	$\gamma^{wag}_{ND_2}$ (amino)	—	—	—	—
42	385	2.1	$\gamma^{wag}_{ND_2}$ (amido), $\gamma^{tw}_{SO_2}$	—	—	—	—
43	372	86.8	$\gamma^{wag}_{ND_2}$ (amido), δ_{CSN}	—	—	—	—
44	357	0.3	$\gamma^{wag}_{ND_2}$ (amino), $\gamma^{wag}_{ND_2}$ (amido), $\gamma^{tw}_{SO_2}$	—	—	—	—
45	322	1.5	δ_{CCC}, v_{PhS}	—	—	—	—
46	291	7.1	$\gamma^{tw}_{ND_2}$ (amino)	—	—	—	—
47	246	2.2	δ_{CSN}, δ_{NPh}	—	—	—	—
48	214	0.4	δ_{NPh}	—	—	—	—
49	150	15.3	$\gamma^{wag}_{NH_2}$ (amino)	—	—	—	—
50	140	8.5	δ_{CSN}, δ_{NPh}	—	—	—	—
51	86	0.4	τ_{sk}	—	—	—	—

^{a} Scaled, according to correlation equation (3) (Table II).

^{b} Vibrational modes: v, stretching; δ, in-plane bending; γ, out-of-plane bending; τ, torsion. Superscripts: s, symmetrical; as, asymmetrical; sc, scissoring; rock, rocking; wag, wagging; tw, twisting. Subscript: sk, skeletal.

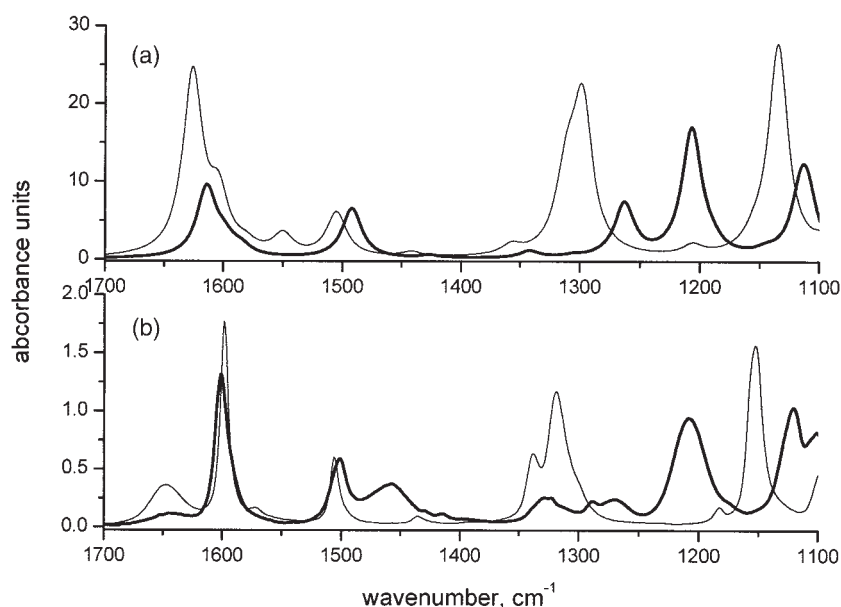^{c} Relative intensities: s, strong; m, moderate; w, weak; v, very.

^{d} $\Delta v_{theor} = v_D - v_H$ (scaled).

^{e} $\Delta v_{exp} = v_D - v_H$.

^{f} $\Delta\Delta v = |\Delta v_{theor} - \Delta v_{exp}|$.

^{g} These bands are inaccessible in the solid-state spectrum of sulfanilamide-d$_0$.

^{h} There are no vibrations with corresponding descriptions in the theoretical spectra of sulfanilamide-d$_0$; cf. Table III.

FIGURE 3. Theoretical (a) and experimental (b) IR spectra of sulfanilamide and its azanion (bold) in DMSO-d$_6$ solutions.

The agreement between theoretical and experimental isotopic shifts for sulfanilamide anion-d$_3$ ($\Sigma\Delta\Delta v_i/\Sigma/v_{i(\exp)}$ = 35.6%, Table VIII) is 2× worse than the corresponding value of 17.4% for sulfanilamide molecule-d$_4$ (Table VI and text in the preceding subsection). The largest individuals deviations

TABLE V _____

Theoretical [B3LYP 6-31++G(d,p)] and experimental (solvent DMSO-d$_6$) IR frequencies (cm^{-1}) and integrated intensities (km mol^{-1}) of sulfanilamide-d$_0$.

No.	B3LYP 6-31++G(d,p)			Experimental data[a]	
	v[b]	A	Approximate description[c]	v	A
9[d]	1626	234	$\delta_{NH_2}^{sc}$ (amino), v_{CC}	1647	47.7
10	1604	69.5	v_{CC}, δ_{PhH}, $\delta_{NH_2}^{sc}$ (amino)	1598	83.5
11	1581	10.1	$v_{CC(Ph)}$, $\delta_{CC(Ph)}$	1574	11.7
12	1550	26.1	$\delta_{NH_2}^{sc}$ (amido)	—[e]	—
13	1505	56.5	δ_{PhH}, $v_{CC(Ph)}$, $v_{C—N}$	1506	29.8
14	1442	6.1	δ_{PhH}, $v_{CC(Ph)}$, $\delta_{NH_2}^{rock}$ (amino)	1435	2.0
15	1357	11.9	$v_{CC(Ph)}$, δ_{PhH}, $\delta_{NH_2}^{rock}$ (amino)	—[f]	—
16	1319	4.9	δ_{PhH}, v_{CC}	—[f]	—
17	1311	92	$v_{C—N}$, $v_{CC(Ph)}$, δ_{PhH}, $v_{C—S}$	—[f]	—
18	1298	187.8	$v_{SO_2}^{as}$, $\delta_{NH_2}^{rock}$ (amido), $v_{CC(Ph)}$	1317	101.9
19	1206	12.2	δ_{PhH}, $v_{C—S}$, δ_{CCC}	1183	1.6
20	1156	12.2	$\delta_{NH_2}^{rock}$ (amino), δ_{PhH}, $v_{CC(Ph)}$	—[f]	—
21	1135	271	$v_{SO_2}^{s}$, δ_{CCC}, $v_{C—S}$	1153	115.3
22[g]	1097	12.9	$\delta_{NH_2}^{rock}$ (amido), v_{CC}	1099	30.9

[a] Measured after having decomposed the complex bands into components.
[b] Scaled, according to correlation equation (2) (Table II).
[c] Vibrational modes: v, stretching; δ, in-plane bending. Superscripts: s, symmetrical; as, asymmetrical; sc, scissoring; rock, rocking.
[d] Preceded by 8 higher-frequency v_{NH_2} and v_{CH} vibrations.
[e] Masked by No. 11.
[f] We did not detect these bands.
[g] Followed by 29 lower-frequency vibrations.

TABLE VI

Theoretical [B3LYP++G(d,p)] and experimental (DMSO-d_6) IR frequencies (v in cm^{-1}), integrated (A in km mol^{-1}) or relative intensities and isotopic shifts Δv (in cm^{-1}) of sulfanilamide-d_4.

No.	B3LYP++G(d,p)			Experimental and other data			
	v^a	A	Approximate description[b]	v^c	Δv_{theor}	Δv_{exp}	$\Delta\Delta v^d$
9[e]	1608	212.5	δ_{PhH}, v_{CC}	1599 vs	4	1	3
10	1578	9.3	δ_{PhH}, v_{CC}	1570 w	−3	−4	1
11	1506	76.6	δ_{PhH}, $v_{C—N}$, v_{CC}	1507 m	1	1	0
12	1435	4.4	δ_{PhH}, v_{CC}	1428 w	−7	−7	0
				(1348) w			
13	1348	154.9	$\delta_{ND_2}^{sc}$ (amino), δ_{PhH}, v_{CC}	1325 w	−278	−322	44
14	1340	17.7	v_{CC}, $\delta_{ND_2}^{sc}$ (amino)	—[f]	−17	—	—
15	1318	0.3	δ_{PhH}	—[f]	−1	—	—
16	1289	194.9	$v_{SO_2}^{as}$, δ_{PhH}	1306 m	−9	−11	2
17	1208	11.4	δ_{PhH}, $\delta_{ND_2}^{sc}$ (amino)	1198 m	2	15	13
18	1184	39.9	$\delta_{ND_2}^{sc}$ (amido), δ_{PhH}, $\delta_{ND_2}^{sc}$ (amino)	1170 m	—[g]	—	—
19	1178	12.6	$\delta_{ND_2}^{sc}$ (amido), $\delta_{ND_2}^{sc}$ (amino), δ_{PhH}	—[f]	—[g]	—	—
20	1149	14	δ_{PhH}	—[f]	7	—	—
21	1129	255.0	$v_{SO_2}^{s}$, $v_{C—S}$, $\delta_{ND_2}^{sc}$ (amido), δ_{CCC}	1146 vs	−6	−7	1
22[h]	1087	79	δ_{CCC}, $v_{SO_2}^{s}$, $\delta_{ND_2}^{sc}$ (amido)	1110 w	—[g]	—	—

[a] Scaled, according to correlation equation (2) (Table II).

[b] Vibrational modes: v, stretching; δ, in-plane bending. Superscripts: s, symmetrical; as, asymmetrical; sc, scissoring.

[c] Relative intensities: s, strong; m, moderate; w, weak; v, very.

[d] $\Delta\Delta v = |\Delta_{theor} - \Delta v_{exp}|$.

[e] Preceded by 8 higher-frequency v_{CH} and v_{ND} vibrations.

[f] These bands were not detected in the experimental spectrum.

[g] There are no vibrations with corresponding descriptions in the theoretical spectra of sulfanilamide-d_0.

[h] Followed by 29 lower-frequency vibrations.

in the present case correspond to the $v_{SO_2}^{as}$ and $v_{SO_2}^{S}$ vibrations. The calculations predict essential decreases of their frequencies caused by the deuteration but, according to the experimental data, these effects are close to zero (Table VIII).

STRUCTURAL ANALYSIS

We shall try to elucidate the steric and electronic structures of sulfanilamide **1a** and its azanion **2a**. The results will make it possible to follow the structural changes caused by the **1a → 2a** conversion.

Steric Structures

The steric structures of the most stable conformers of sulfanilamide and its azanion are shown in Figure 1; the numerical theoretical and experimental (X-ray diffraction for **1a** only [31–33]) values of the corresponding parameters are compared in Table IX.

We can see in Table IX very good agreement between theoretical and experimental bond lengths

of sulfanilamide molecule: the mean absolute deviation (m.a.d.) between them is 0.019 Å. The largest individual deviation of 0.077 Å corresponds to the S^8—N^{11} bond and can be related to the formation of hydrogen bonds in the crystal state. The m.a.d. value with respect to the bond angles is 1.41° (Table IX). The results obtained can be considered very good, with m.a.d. values comparable to the average experimental errors (0.01–0.02 Å and 1°–2° [31–33]). In contrast, no one could expect full coincidence between experimental data for the crystal state and theoretical values, computed for an isolated sulfanilamide molecule.

There are no experimental structural data for sulfanilamide azanion. The calculations predict (Table IX, last column) that the largest structural variations, caused by the **1a → 2a** conversion, should take place both at (shortening of the S^8—N^{11} bond by 0.120 Å) and next to it (lengthening of the C^4—S^8 bond by 0.056 Å). This rule is also valid for the bond angles (Table IX); it agrees with the data for carbanions, oxyanions, and other azanions (Refs. [10, 13, 14, 19, 34] and references therein).

TABLE VII

Theoretical [B3LYP++G(*d,p*)] and experimental (solvent DMSO-d$_6$, counter ion Na$^+$) IR frequencies (v in cm^{-1}), integrated intensities (A in km mol^{-1}) of sulfanilamide azanion-d$_0$.

No.	B3LYP++G(*d,p*)			Experimental data[a]	
	v[b]	A	Approximate description[c]	v	A
8[d]	1614	89	$\delta_{NH_2}^{sc}$, v_{CC}	1648	8.4
9	1599	18.2	v_{CC}, δ_{PhH}, $\delta_{NH_2}^{sc}$ (amino)	1600	103.5
10	1585	10.2	v_{CC}, δ_{CCC}	—[e]	—[e]
11	1492	64.2	δ_{PhH}, v_{CC}, $v_{C—N}$	1502	45.8
12	1426	3.4	δ_{PhH}, v_{CC}, $\delta_{NH_2}^{rock}$ (amino)	1460	54.0
13	1342	8.8	v_{CC}, δ_{PhH}, $\delta_{NH_2}^{rock}$ (amino)	1326	22.8
14	1306	2.3	v_{CC}, δ_{PhH}	1289	14.6
15	1263	68.4	$v_{C—N}$, v_{CC}, δ_{PhH}	1269	12.8
16	1207	163.6	$v_{SO_2}^{as}$, v_{CC}, δ_{SNH}	1208	134.5
17	1191	10.4	δ_{PhH}, v_{CC}	—[e]	—[e]
18	1145	6	δ_{PhH}, $\delta_{NH_2}^{rock}$ (amino), δ_{SNH}	—[e]	—[e]
19	1115	82.3	$v_{SO_2}^{s}$, δ_{SNH}, v_{CC}	1122	86.3
20[f]	1109	48.2	δ_{CCC}, δ_{SNH}, $v_{C—S}$	1100	87.2

[a] Measured after having decomposed the complex bands into components.
[b] Scaled according to correlation equation (2) (Table II).
[c] Vibrational modes: v, stretching; δ, in-plane bending. Superscripts: s, symmetrical; as, asymmetrical; sc, scissoring; rock, rocking.
[d] Preceded by 7 higher-frequency v_{NH} and v_{CH} vibrations.
[e] This bands were not detected in the experimental spectrum.
[f] Followed by 28 lower-frequency vibrations.

TABLE VIII

Theoretical [B3LYP++G(*d,p*)] and experimental (solvent DMSO-d$_6$, counter ion Na$^+$) IR frequencies (v in cm^{-1}) and integrated (A in km mol^{-1}) or relative intensities and isotopic shifts Δv (in cm^{-1}) of sulfanilamide azanion-d$_3$.

No.	B3LYP++G(*d,p*)			Experimental and other data			
	v[a]	A	Approximate description[b]	v[c]	Δv_{theor}	Δv_{exp}	$\Delta\Delta v$[d]
8[g]	1601	56.6	v_{CC}, δ_{PhH}	1601 w	−2	—	2
9	1579	7.4	v_{CC}, δ_{PhH}	—[e]	—	—	—
10	1492	77.3	δ_{PhH}, v_{CC}	1501 s	0	−1	1
11	1415	1.6	δ_{PhH}, v_{CC}	1462 w	−11	2	13
12	1325	10.6	v_{CC}, δ_{PhH}	1327 m	−17	1	16
13	1305	10.6	δ_{PhH}	—[e]	—	—	—
14	1298	117.7	$\delta_{ND_2}^{sc}$ (amino), δ_{PhH}, v_{CC}, δ_{PhH}	1289 w	−331	−359	28
15	1192	7.4	δ_{PhH}	—[e]	—	—	—
16	1183	222.6	$v_{SO_2}^{as}$, δ_{SNH}, δ_{PhH}	1209 vs	−27	1	28
17	1173	7.3	δ_{PhH}, $\delta_{ND_2}^{sc}$ (amino)	1150 w	—[f]	—	—
18	1127	29.5	δ_{PhH}	—[e]	—	—	—
19	1109	66.6	δ_{CCC}, $v_{SO_2}^{s}$, v_{CC}	110 s	0	0	0
20[h]	1074	270.6	$v_{SO_2}^{s}$, δ_{CCC}, v_{CC}, v_{NS}	1121 s	−43	−1	42

[a] Scaled, according to correlation equation (2) (Table II).
[b] Vibrational modes: v, stretching; δ, in-plane bending. Superscripts: s, symmetrical; as, asymmetrical; sc, scissoring.
[c] Relative intensities: s, strong; m, moderate; w, weak; vs, very strong.
[d] $\Delta\Delta v = |\Delta_{theor} - \Delta v_{exp}|$.
[e] These bands were not detected in the experimental spectrum.
[f] There is no vibration with corresponding descriptions in the theoretical spectra of sulfanilamide-d$_3$.
[g] Preceded by 7 higher-frequency v_{NH} and v_{CH} vibrations.
[h] Followed by 29 lower-frequency vibrations.

TABLE IX

Theoretical [B3LYP++G(*d,p*)] and experimental (X-ray diffraction [31–33]) bond lengths (Å) and angles (degrees) of the molecule 1a and azanion 2a of sulfanilamide.

| Bonds and angles[a] | Molecule | | Anion | | |
	X-ray[b]	B3LYP	Δ[c]	B3LYP	∇[d]
C^1C^2	1.377	1.389	0.012	1.395	0.006
C^1C^3	1.393	1.410	0.017	1.404	−0.006
C^2C^4	1.402	1.399	−0.003	1.399	0.000
C^3C^5	1.409	1.409	0.000	1.401	−0.008
C^3—N^7	1.388	1.386	−0.002	1.419	0.033
C^4C^6	1.395	1.398	0.003	1.396	−0.002
C^4—S^8	1.743	1.783	0.040	1.839	0.056
C^5C^6	1.382	1.391	0.009	1.399	0.008
S^8=O^9	1.430	1.470	0.050	1.49	0.020
S^8=O^{10}	1.454	1.470	0.016	1.502	0.032
S^8—N^{11}	1.635	1.702	0.067	1.582	−0.120
m.a.d.[e]	—	—	*0.019*	—	—
C^2—C^1—C^3	120.6	120.64	0.04	120.56	−0.08
C^4—S^8—O^9	108.0	108.33	0.33	102.74	−5.59
C^4—S^8—O^{10}	107.3	107.58	0.28	102.43	−5.15
C^4—S^8—N^{11}	108.8	104.30	−4.50	108.25	3.95
O^9—S^8—O^{10}	118.1	122.16	4.06	116.71	−5.45
O^9—S^8—N^{11}	107.4	105.40	−1.99	110.17	4.77
C^1—C^3—N^7	120.7	118.78	−1.92	120.57	1.79
C^5—C^3—N^7	119.6	118.78	−0.82	120.77	1.99
C^2—C^4—C^6	119.6	120.46	0.86	118.81	−1.65
C^2—C^4—S^8	120.2	119.71	−0.49	120.04	0.33
C^6—C^4—S^8	120.1	119.83	−0.27	121.09	1.26
C^3—C^5—C^6	118.2	120.63	2.43	120.52	−0.11
O^{10}—S^8—N^{11}	106.0	107.70	1.70	115.11	7.41
C^1—C^2—C^4	119.7	119.75	0.05	120.74	0.99
m.a.d.[e]	—	—	*1.41*	—	—

[a] For the atom numbering, see Scheme 2.
[b] Mean values for three polymorphic forms [31–33].
[c] Algebraic deviations (Å, degrees) between theoretical and experimental values.
[d] Algebraic deviations (Å, degrees) between theoretical values of the anion and molecule.
[e] Mean absolute deviation between theoretical and experimental values.

Electronic Structures

The net Mulliken electric charges q_i over fragments of the molecule **1a** and azanion **2a** of sulfanilamide are shown in Scheme 2. The charge change values $\Delta q_i = q_i$ (anion) $- q_i$ (molecule) are usually quite informative in showing the distribution of the new (e.g., carbanionic, azanionic) changes in anions (Refs. [10, 11, 13, 14, 19, 20, 28, 29, 34] and references therein). According to the present calculations, the new (azanionic) charge of **2a** is distributed, as follows: 0.08e⁻, 0.23e⁻, and 0.12e⁻ are delocalized over the amino, phenylene, and sulfonyl groups, respectively, and

0.57e⁻ remain localized at the azanionic center (cf. Scheme 2).

We believe that the calculated net charges of **1a** are not from the real ones, based on the following
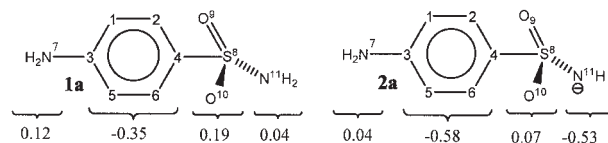
SCHEME 2. Net Mulliken electric charges q_i of fragments of the molecule **1a** and azanion **2a** of sulfanilamide.

criteria: (i) we calculated a dipole moment of sulfanilamide μ of 5.18 Debye; (ii) the following μ values (in Debye) of this molecule were found: 7.1 (pyridine, 25°C), 6.60 (dioxane, 25°C), 6.22 (benzene/dioxane, 25°C) [35–37]; and (iii) all the experimental values are larger than the theoretical one, but the order of their increase corresponds to the increase in the ability of the solvents to form strong hydrogen bonds with the sulfanilamide molecule.

Conclusion

The comparisons, performed in this work between experimental (in cases where they are available) and B3LYP 6-31++G(*d,p*) data, showed good agreement for the IR spectral changes, caused by the molecule → azanion conversion, and a very good agreement for the structural data of the sulfanilamide molecule. We anticipate that the structural data, predicted by the same theoretical method for sulfanilamide azanion and (therefore) the structural changes, accompanying the above conversions should also be adequate.

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