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DFT study of *N*-substituted sulfamic acid derivatives acidity in aqueous media and gas phase

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Abstract. Sulfamic acids are very important compounds with a little consideration in the literature that have wide range of applications in our life. Various *N*-alkyl and *N*-cycloalkyl sulfamic acids were selected and their acidity was calculated in gas and aqueous media. *pKa* values were obtained with the use of two thermodynamic cycles that differ in the reference molecule which was used with them. Obtained *pKa* values show strong acidity for sulfamic acids. We used density functional theory for all calculations.

1. Introduction

Sulfamic acid is a colorless, water-soluble compound with the formula of H_3NSO_3, and is referred to as amidosulfonic acid in the older literature, but is now generally known as sulfamic acid. Sulfamic acid was first isolated by Berglund in 1878, but was not considered by chemists until that a comparatively simple method for its preparation was proposed [1,2].

Sulfamic acid is used as an acidic cleaning agent for metals and ceramics. It is frequently used for removing rust and limescale, instead of more volatile and irritating hydrochloric acid. It is also used as catalyst in organic synthesis [3-7], dye and pigment synthesis, as an ingredient for fire extinguishing materials and chloride stabilizer in paper industry, synthesis of nitrous oxide by reaction with nitric acid [1,2].

Sulfamic acid has many different derivatives that differ in alkyl group exchanged with a hydrogen atom of amine. *N*-alkyl sulfamic acids and their salts are important chemicals that have many applications, such as artificial sweeteners. Sodium cyclamate is a sodium salt of *N*-cyclohexyl sulfamic acid that has an important role in the food industry as artificial sweetener [8].

Some of the other applications of sulfamic acid salts include using in the design and synthesis of many various types of therapeutic agents such as antibiotics, anti-cancer drugs (steroid sulfatase and carbonic anhydrase inhibitors), HIV protease inhibitors (PIs), nucleoside/nucleotide Human Immunodeficiency Virus (HIV) reverse transcriptase inhibitors, anti-epileptic drugs, and weight loss drugs [9].

Acidity is the most important characteristic properties of these compounds that plays main role in their application capabilities. By reviewing existing literature we find that quantum mechanical methods successfully had been used for ab initio *pKa* value calculation and other thermodynamic data in the case of many various organic and inorganic acids [10-15]. For instance, lots of papers were published annually in that field [16-22]. In many works, researchers try to correlate *pKa* values of acids with theoretical descriptor, and in many cases good correlation has been obtained [10,23]. Many researchers have investigated gas phase and solution phase acidities of a number of organic compounds [12,24,25]. They have shown that calculations of *pKa* values with the use of ab-initio methods for acids correlate were well satisfied with the

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experimental data [26-28]. However, the sulfamic acids have not yet been considered in detail. Because of important applications of sulfamic acid derivatives in industrial and drug chemistry and lack of useful data about their structure and termochemistry in literature, we start a research work on sulfamic acid derivatives using computational chemistry. Therefore, in this study, we have computed the relative pKa values of several sulfamic acids using density functional theory methods at B3LYP/6-31++G (d,p) level.

2. Methods and theoretical considerations

Calculation of pKa value for dissociation of an acid is possible with the use of the changing in free energy of the following reaction [14,23]:

$$HA_{(aq)} + \mathrm{H_2O}_{(aq)} \xrightarrow{\Delta G^0} A^-_{(aq)} + \mathrm{H_3O}^+_{(aq)}, \qquad (1)$$

$$\Delta G^0 = -2.303RT\log(Ka/[\mathrm{H_2O}]), \qquad (2)$$

or:

$$\Delta G^0 \text{ (kcal/mol)} = 1.36pKa + 2.36, \qquad (3)$$

where ΔG^0 is the free energy changing for the dissociation Reaction (1) at 298 K with concentration of 1 mol/L that corresponds to standard state. 1.36 and 2.36 are the values acquired from replacing the R and T values in $-2.303RT$ and $2.303RT\log(55.56)$, respectively. Change in free energy can be computed using gas phase free energies and solvation energies for the dissociation Reaction (1) [26]. We can compute the gas phase Gibbs free energies by applying thermal corrections arising from nuclear motions (translational, rotational and vibrational) on internal electronic energies using one atmosphere as a standard state [27]. Polarized Continuum Model (PCM) can be used for calculation of solvation energies with considering changing on standard state of one atmosphere for gas phase to 1 mol/L for solution phase [28]. Molecular free energy in the solution is calculated as follows by use of the PCM model:

$$G_{\mathrm{sol}} = G_{\mathrm{es}} + G_{\mathrm{dr}} + G_{\mathrm{cav}},$$

where the (es), (dr) and (cav) subscripts represent the electrostatic, the dispersion-repulsion, and the cavitation energy contributions to free energy, respectively. All of the above mentioned terms could be calculated using a cavity defined based on van der Wals radii.

In this study, in order to calculate solution phase acidity (pKa) values, we have used two Thermodynamic Cycles (TC) that differ only in the used reference molecule.

TC (A): Isodesmic Reaction (4) and the dissociation of sulfamic acid (HSA), as a reference molecule (5), were combined using thermodynamic cycle (A) (Figure 1) for ΔG^0 calculation of Reaction (1):

$$\begin{tikzcd}
HA_{(g)} \arrow[d, "\Delta G_{(\mathrm{sol}.HA)}"] & + & SA^-_{(g)} \arrow[r, "\Delta G^0_{4(\mathrm{gas})}"] \arrow[d, "\Delta G_{(\mathrm{sol}.SA-)}"] & A^-{}_{(g)} \arrow[d, "\Delta G_{(\mathrm{sol}.A-)}"] & + & HSA_{(g)} \arrow[d, "\Delta G_{(\mathrm{sol}.HSA)}"] \\
HA_{(\mathrm{aq})} & + & SA^-_{(\mathrm{aq})} \arrow[r, "\Delta G^0_{4(\mathrm{aq})}"] & A^-{}_{(\mathrm{aq})} & + & HSA_{(\mathrm{aq})}
\end{tikzcd}$$

Figure 1. Proposed thermodynamic cycle (A).

$$HA_{(aq)} + SA^-_{(aq)} \xrightarrow{\Delta G^0_{4(aq)}} A^-_{(aq)} + HSA_{(aq)}, \qquad (4)$$

$$HSA_{(aq)} + \mathrm{H_2O}_{(aq)} \xrightarrow{\Delta G^0_{5(aq)}} SA^-_{(aq)} + \mathrm{H_3O}^+_{(aq)}. \qquad (5)$$

In aqueous solution, the Gibbs free energy Δ, G^0, of dissociation of acid HA, can be written as a sum of Gibbs free energy changes of Reactions (4) and (5):

$$\Delta G^0 = \Delta G^0_{4(aq)} + \Delta G^0_{5(aq)}. \qquad (6)$$

By considering the experimental value of pKa, 1.05 [29], $\Delta G^0_{5(aq)}$ can be easily calculated using Eq. (3) as:

$$\Delta G^0_{5(aq)} = 1.36(1.05) + 2.36 = 3.72 \quad \text{(kcal/mol)}.$$

Figure 1 shows the thermodynamic cycle proposed to calculate the $\Delta G^0_{4(aq)}$.

According to this cycle, $\Delta G^0_{4(aq)}$ can be written as the sum of $\Delta G^0_{4(\mathrm{gas})}$ and $\Delta\Delta G^0_{(\mathrm{sol})}$ in which $\Delta G^0_{4(\mathrm{gas})}$ and $\Delta\Delta G^0_{(\mathrm{sol})}$ are the gas-phase Gibbs free energy of Reaction (4), and the net solvation energy of Reaction (4), respectively:

$$\Delta G^0_{4(aq)} = \Delta G^0_{4(\mathrm{gas})} + \Delta\Delta G^0_{(\mathrm{sol})}. \qquad (7)$$

The gas-phase Gibbs free energy, $\Delta G^0_{4(\mathrm{gas})}$, of Reaction (4), and the net solvation energy, $\Delta G^0_{4(aq)}$, of Reaction (4) are defined as:

$$\Delta G^0_{4(\mathrm{gas})} = \left[G^0_{(\mathrm{gas},A-)} + G^0_{(\mathrm{gas},HSA)}\right] - \left[G^0_{(\mathrm{gas},HA)} + G^0_{(\mathrm{gas},SA-)}\right], \qquad (8)$$

$$\Delta\Delta G^0_{(\mathrm{sol})} = \left[\Delta G^0_{(\mathrm{sol},A-)} + \Delta G^0_{(\mathrm{sol},HSA)}\right] - \left[\Delta G^0_{(\mathrm{sol},HA)} + \Delta G^0_{(\mathrm{sol},SA-)}\right]. \qquad (9)$$

Replacing $\Delta G^0_{4(aq)}$ and $\Delta G^0_{5(aq)}$ in Eq. (6) results in:

$$\Delta G^0 \text{ (kcal/mol)} = 1.36pKa + 2.36$$
$$= \left[G^0_{(\text{gas},A^-)} + G^0_{(\text{gas},HSA)}\right]$$
$$- \left[G^0_{(\text{gas},HA)} + G^0_{(\text{gas},SA^-)}\right]$$
$$+ \left[\Delta G^0_{(\text{sol},A^-)} + \Delta G^0_{(\text{sol},HSA)}\right]$$
$$- \left[\Delta G^0_{(\text{sol},HA)} + \Delta G^0_{(\text{sol},SA^-)}\right] + 3.72. \tag{10}$$

By reforming of Eq. (10), we obtain an expression for calculation of pKa as:

$$pKa = \left\{ \left[G^0_{(\text{gas},A^-)} + G^0_{(\text{gas},HSA)}\right] - \left[G^0_{(\text{gas},HA)} + G^0_{(\text{gas},SA^-)}\right] + \left[\Delta G^0_{(\text{sol},A^-)} + \Delta G^0_{(\text{sol},HSA)}\right] - \left[\Delta G^0_{(\text{sol},HA)} + \Delta G^0_{(\text{sol},SA^-)}\right] + 1.36 \right\} / 1.36. \tag{11}$$

By replacing the calculated data for the reference molecule (HSA) and its conjugated anion (SA^-), Eq. (11) can be written in the simple form:

$$pKa = \left\{ \left[G^0_{(\text{gas},A^-)} + G^0_{(\text{gas},HA)}\right] + \left[\Delta G^0_{(\text{sol},A^-)} - \Delta G^0_{(\text{sol},HA)}\right] - 260.67 \right\} / 1.36. \tag{12}$$

Subsequently, Eq. (12) is used for pKa calculation when we use (HSA) as a reference molecule.

TC (B): Thermodynamic cycle, as shown in Figure 2, presents a method for calculation of the Gibbs free energy of Reaction (1) using H_2O as a reference molecule. Therefore, using this direct TC in order to calculate Gibbs free energy needs the Gibbs free energies of H_2O and H_3O^+ in solution, which should be calculated. Calculated gas phase Gibbs free energies and solvation energies of H_2O and H_3O^+ are collected in Table 1.

Isodesmic Reaction (13) and the dissociation of H_3O^+ as a reference molecule (14) were combined using thermodynamic cycle (B) (Figure 2) for ΔG^0 calculation of Reaction (1):

$$HA_{(aq)} + H_2O_{(aq)} \xrightarrow{\Delta G^0_{13(aq)}} A^-_{(aq)} + H_3O^+_{(aq)}, \tag{13}$$

$$H_3O^+_{(aq)} + H_2O_{(aq)} \xrightarrow{\Delta G^0_{14(aq)}} H_2O_{(aq)} + H_3O^+_{(aq)}. \tag{14}$$

ΔG^0 can be written as sum of $\Delta G^0_{13(aq)}$ and $\Delta G^0_{14(aq)}$:

$$\Delta G^0 = \Delta G^0_{13(aq)} + \Delta G^0_{14(aq)}. \tag{15}$$

$\Delta G^0_{14(aq)}$ can be obtained by Eq. (3) and considering the experimental value of pKa, i.e. -1.74 [30] as:

$$\Delta G^0_{14(aq)} = 1.36(-1.74) + 2.36 = 0.00 \quad \text{(kcal/mol)}. \tag{16}$$

Figure 2 shows the thermodynamic cycle proposed to calculate the $\Delta G^0_{13(aq)}$. From this cycle, $\Delta G^0_{13(aq)}$ is given by the expression:

$$\Delta G^0_{13(aq)} = \Delta G^0_{13(\text{gas})} + \Delta\Delta G^0_{(\text{sol})}, \tag{17}$$

in which $\Delta G^0_{13(\text{gas})}$ is the gas-phase Gibbs free energy of reaction and is defined as:

$$\Delta G^0_{13(\text{gas})} = \left[G^0_{(\text{gas},A^-)} + G^0_{(\text{gas},H_3O^+)}\right] - \left[G^0_{(\text{gas},HA)} + G^0_{(\text{gas},H_2O)}\right], \tag{18}$$

$$\Delta\Delta G^0_{(\text{sol})} = \left[\Delta G^0_{(\text{sol},A^-)} + \Delta G^0_{(\text{sol},H_3O^+)}\right] - \left[\Delta G^0_{(\text{sol},HA)} + \Delta G^0_{(\text{sol},H_2O)}\right]. \tag{19}$$

Replacing $\Delta G^0_{13(aq)}$ and $\Delta G^0_{14(aq)}$ in Eq. (15) results

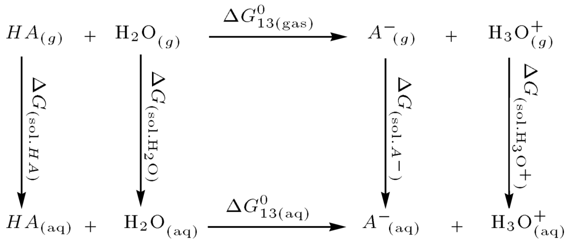


Figure 2. Proposed thermodynamic cycle (B).

Table 1. Calculated gas phase Gibbs free energies and solvation energies of H_2O and H_3O^+.

Entry	**H_2O**	**H_3O^+**
Gas phase Gibbs free energy (Hartree)	-76.454884	-76.714206
Solvation energies (kcal/mol)	-6.67	-105.30

in:

$$\begin{aligned}\Delta G^0 \text{ (kcal/mol)} =& 1.36pKa + 2.36\\ =& \left[G^0_{(\text{gas},A^-)} + G^0_{(\text{gas},\text{H}_3\text{O}^+)}\right]\\ &- \left[G^0_{(\text{gas},HA)} + G^0_{(\text{gas},\text{H}_2\text{O})}\right]\\ &+ \left[\Delta G^0_{(\text{sol},A^-)} + \Delta G^0_{(\text{sol},\text{H}_3\text{O}^+)}\right]\\ &- \left[\Delta G^0_{(\text{sol},HA)} + \Delta G^0_{(\text{sol},\text{H}_2\text{O})}\right].\end{aligned} \tag{20}$$

By reforming Eq. (20), an expression for pKa calculation is obtained as:

$$\begin{aligned}pKa =& \Big\{ \left[G^0_{(\text{gas},A^-)} + G^0_{(\text{gas},\text{H}_3\text{O}^+)}\right]\\ &- \left[G^0_{(\text{gas},HA)} + G^0_{(\text{gas},\text{H}_2\text{O})}\right]\\ &+ \left[\Delta G^0_{(\text{sol},A^-)} + \Delta G^0_{(\text{sol},\text{H}_3\text{O}^+)}\right]\\ &- \left[\Delta G^0_{(\text{sol},HA)} + \Delta G^0_{(\text{sol},\text{H}_2\text{O})}\right] - 2.36\Big\}/1.36.\end{aligned} \tag{21}$$

By replacing the calculated data for the reference molecule H_3O^+ and its conjugated anion H_2O, Eq. (21) can be written in the simple form:

$$\begin{aligned}pka =& \Big\{ \left[G^0_{(\text{gas},A^-)} + G^0_{(\text{gas},HA)}\right]\\ &+ \left[\Delta G^0_{(\text{sol},A^-)} - \Delta G^0_{(\text{sol},HA)}\right] - 263.73\Big\}/1.36.\end{aligned} \tag{22}$$

Afterwards, Eq. (22) is used for calculation of pKa when we use H_3O^+ as a reference molecule.

Calculation of pKa, using Eqs. (12) and (22), needs values of $G^0_{(\text{gas},A^-)}$, $G^0_{(\text{gas},HA)}$, $\Delta G^0_{(\text{sol},A^-)}$ and $\Delta G^0_{(\text{sol},HA)}$. To reach this goal, the gas phase Gibbs free energies and solvation energies have been determined from the density functional theory at the level of B3LYP. Solvation energies $\Delta G^0_{(\text{sol},i)}$ have been calculated using Integral Equation Formalism Polarizable Continuum Model (IEF-PCM) and SCFVAC keyword because it is less sensitive to diffuse solute charge distribution. By default, the PCM method builds up the cavity using a United Atom (UA) model, i.e. by putting a sphere around each solute heavy atom. We have used UAHF radii (United Atom Topological Model) for IEF-PCM calculations which use the united atom topological model applied on radii optimized for the HF/6-31G (d) level of theory. These are the recommended radii for the calculation of solvation Gibbs free energy via the SCFVAC PCM keyword. By considering the structure of selected molecules and recommendations about anions and molecules with non-bonding lone pair electrons, the 6-311++G (d,p) has been chosen as diffuse basis set [31]. All of the studied molecular structures were fully optimized. Gaussian 03 was employed for all DFT calculations [32].

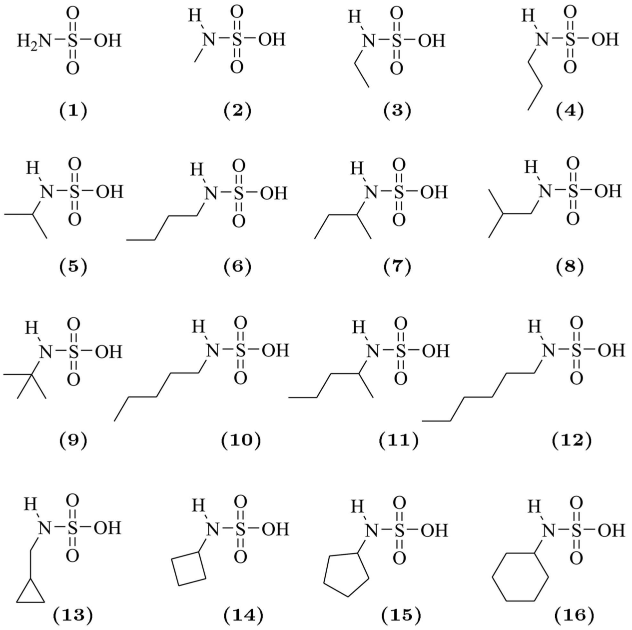


Figure 3. Studied sulfamic acid structures.

3. Results and discussion

We chose fifteen N-alkyl and cycloalkyl sulfamic acids in our study. Structures of selected molecules are shown in Figure 3. Experimental pKa value was found only for sulfamic acid which was $pKa = 1.05$ [29,33]. Table 2 shows the calculated gas phase energy and solvation energy of each acid and its corresponding anion together with the standard Gibbs free energy of Reaction (1), ΔG^0 and pKa values which were computed with two methods using Eqs. (12) and (22).

The results obtained using two different methods were different. In TC (A) some of systematic errors that exist in the Gibbs free energy calculation will be cancelled in the case of Gibbs free energy determination of proton transfer reaction. Therefore we can expect that obtained results to be reliable. But because of using a reference molecule, these results will be reference dependencies [34]. We chose the non-substituted sulfamic acid as reference; however, one can change it with another one in order to improve the results. Results obtained from TC (B) are reference-independent because the water molecule is used. This method is more compatible with experiment, but some problems

Table 2. Gas and solution phase Gibbs free energy of acids and their anions together with calculated pKa values and gas phase acidity (ΔH_1).

Comp.	$\Delta G^0_{i(\mathrm{gas})}$ (Hartree) acid	$\Delta G^0_{i(\mathrm{gas})}$ (Hartree) anion	$\Delta G^0_{i(\mathrm{sol})}$ (kcal/mol) acid	$\Delta G^0_{i(\mathrm{sol})}$ (kcal/mol) anion	ΔG^0_1 (kcal/mol) Meth.1	pKa (kcal/mol) Meth.1	ΔG^0_1 (kcal/mol) Meth.2	pKa (kcal/mol) Meth.2	ΔH_1 (kcal/mol)
1	-680.445757	-679.943736	-17.2	-69.1	1.7	-0.5	-	-	316.0
2	-719.735386	-719.232724	-15.8	-67.0	2.9	0.4	5.9	2.6	316.2
3	-759.037119	-758.533061	-15.3	-65.2	5.0	1.9	8.1	4.2	317.0
4	-798.338513	-797.831966	-13.3	-63.8	6.0	2.7	9.1	4.9	318.0
5	-798.338642	-797.834986	-14.4	-63.5	5.1	2.0	8.7	4.7	316.7
6	-837.635454	-837.131407	-14.4	-64.2	5.1	2.0	8.2	4.3	317.2
7	-837.637505	-837.133829	-12.9	-60.4	7.2	3.5	10.3	5.8	316.9
8	-837.635900	-837.132717	-13.2	-61.7	5.8	2.5	8.9	4.8	316.7
9	-837.636286	-837.131170	-13.2	-61.4	7.4	3.7	10.5	6.0	317.8
10	-876.933505	-876.430164	-14.2	-63.7	5.0	1.9	8.1	4.2	317.1
11	-876.933273	-876.429709	-13.4	-62.7	5.3	2.2	8.4	4.4	317.4
12	-916.232158	-915.728387	-14.1	-63.4	6.5	3.0	8.5	4.5	317.2
13	-836.408260	-835.905643	-13.8	-63.7	4.7	1.7	7.1	3.5	316.2
14	-836.411546	-835.909133	-15.1	-64.0	4.9	1.9	8.0	4.1	316.1
15	-875.735442	-875.231182	-14.8	-63.5	6.4	2.9	9.4	5.2	317.2
16	-915.040186	-914.536547	-14.6	-62.8	6.5	3.0	9.5	5.3	317.0

related to acquiring the Gibbs free energy of solvation of H_3O^+ may seriously affect the results [35,36].

The pKa results obtained in this study can be used to acquire some information about the acidity of different N-alkyl sulfamic acids. There are three factors that affect the acidity of various N-alkyl sulfamic acids:

1. The size of alkyl group: For example, methyl sulfamic acid has a smaller pKA than ethyl sulfamic acid. This may be attributed to the increasing positive inductive effect of alkyl group as its size increases. Another example can be seen in the case of cyclo-alkyl substituted sulfamic acids in which their pKa values increase from cyclo-butyl to cyclo-hexyl derivative.
2. The number of branches on alkyl group: For example, between N-butyl, Sec-butyl and Tert-butyl sulfamic acids, pKa values increased from N-butyl to Tert-butyl derivative.
3. Solvation of ion: This depends on the size of alkyl groups which generally decreases with increasing the size of alkyl group in aqueous media because of differences in the nature of inter molecular forces.

The solubility, polarity and solvation of sulfamic acid decrease as the size and the number of alkyl group increase. Higher pKa value for N-propyl sulfamic acid in comparison with N-butyl or N-pentyl derivatives may be due to the difference in their solvation capability.

$$HA_{(g)} \rightarrow A^-_{(g)} + H^+_{(g)}$$

Scheme 1. Gas phase acid dissociation.

Last column of Table 2 lists the enthalpy values of acid dissociation of various sulfamic acids (gas phase acidity) calculated from Eq. (26) as follows (Scheme 1):

$$\Delta H_1 = \Delta U_1 + \Delta(PV) = U_{(A^-)} + U_{(H^+)} - U_{(HA)} + RT, \tag{23}$$

$$\Delta H_1 = \Delta U_1 + \Delta(PV) = U_{(A^-)} - U_{(HA)} + 2.5RT, \tag{24}$$

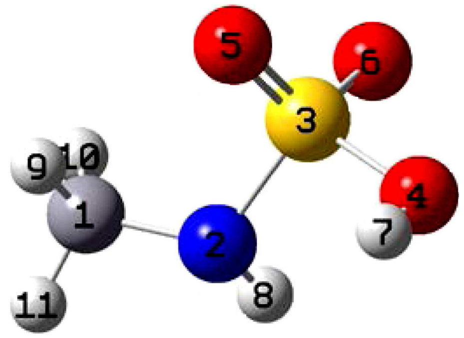
$$\Delta H_1 = U_{(A^-)} - U_{(HA)} + 2.5(0.0019858775\ \text{kcal/molK})(298.15\ \text{K}), \tag{25}$$

$$\Delta H_1 = U_{(A^-)} - U_{(HA)} + 1.48\ (\text{kcal/mol}). \tag{26}$$

In Eq. (23) we substituted $\Delta(PV)$ with RT (one mole of gas is obtained in the Reaction (1)) and $U_{(H^+)}$with a $1.5RT$.

Tables 3 and 4 enlist some selected bond lengths, angles and dihedral angles of various sulfamic acids in neutral and anion forms. As results show d_{1-2}, d_{3-5} and d_{3-6} in all sulfamic acid derivatives have nearly equal value for two forms but d_{2-3} and d_{3-4}

Table 3. Selected bond lengths of some sulfamic acids in neutral and anionic forms.



Comp.	**Form**	d_{1-2}	d_{2-3}	d_{3-4}	d_{3-5}	d_{3-6}
1	neutral	-	1.68	1.627	1.44	1.45
1	anion	-	1.756	1.489	1.479	1.479
3	neutral	1.481	1.678	1.632	1.447	1.451
3	anion	1.463	1.750	1.490	1.479	1.480
7	neutral	1.486	1.667	1.635	1.446	1.452
7	anion	1.469	1.750	1.490	1.480	1.480
9	neutral	1.501	1.669	1.635	1.446	1.453
9	anion	1.479	1.758	1.490	1.481	1.474
12	neutral	1.478	1.674	1.634	1.446	1.451
12	anion	1.462	1.755	1.489	1.479	1.480
15	neutral	1.481	1.671	1.635	1.446	1.452
15	anion	1.463	1.751	1.490	1.479	1.480
16	neutral	1.487	1.678	1.634	1.447	1.451
16	anion	1.465	1.754	1.490	1.481	1.478

Table 4. Selected bond angles and dihedral angles of various sulfamic acids in neutral form.

Comp.	$<1-2-3$	$<2-3-4$	$<3-4-7$	$<4-3-6$	$<1-2-3-6$	$<2-3-4-7$	$<6-3-4-7$
1	109.8	100.3	109.5	109.5	36.2	-68.4	42.5
2	116.3	99.0	109.1	110.0	48.2	-67.9	43.4
3	118.1	99.7	109.1	109.6	-40.6	66.4	-45.2
4	120.7	101.2	108.5	106.3	50.7	155.2	40.6
5	118.4	99.5	109.0	109.6	-42.9	66.7	-44.8
6	118.1	100.6	108.8	109.3	-164.9	69.3	-41.9
7	120.2	101.0	108.9	109.3	164.2	-67.7	43.6
8	118.1	100.5	108.8	109.4	-80.5	-69.0	42.1
9	124.4	102.1	108.8	108.4	-157.5	68.4	-42.5
10	119.7	97.8	107.3	105.7	30.0	147.0	30.0
11	118.1	100.6	108.8	109.3	164.7	-69.3	42.0
12	118.0	100.5	108.8	109.3	165.2	-69.4	41.9
13	116.6	99.2	109.0	109.9	49.2	-68.5	43.0
14	117.6	99.4	109.0	109.7	-44.6	67.3	-44.3
15	119.8	100.6	108.8	109.4	-165.8	68.0	-43.0
16	118.3	99.5	109.0	109.6	43.4	-66.3	45.3

are different. Resonance of nitrogen lone pair electrons with sulfur atom could increase N-S bond order. In comparison with neutral and anionic forms, the latter one has longer N-S bond because the negative charge on the oxygen atom causes the resonance of non bonding electrons of the nitrogen atom to decrease. The resonance leads to higher d_{3-4} bond length in anionic form as compared with d_{3-4} bond in the neutral structure.

4. Conclusion

In this study, we present two general equations for calculation of pKa sulfamic acids. We calculated relative pKa values in gas and solution phase for a limited number of sulfamic acid derivatives. As the results show the strength of acidity can be affected by substitution type and size. Some selected structural data such as bond lengths, angles, and dihedral angles for studying molecules were also calculated.

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