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Theoretical Investigations on $R(O)_nS - NH_2$ (n=0,1,2) systems

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In the current article, *ab initio* study on the stability of Sulfenamide (1) and its oxidized derivatives (2 and 3) has been reported. The bond length, rotational barrier, inversion barrier and negative hyper conjugative interactions have been calculated using *ab initio* MO and Density Functional (DFT) calculations and their values are compared. The analysis showed that negative hyperconjugative interactions play important role in these molecules.

Keyword: Sulfenamide, sulfinamide, sulfonamide, negative hyper conjugation

1. Introduction

Organosulfur compounds with S-N bonds have wide range of applications including medicinal [1]. There are more than 30 drugs in wide use which contain sulfonamide $RO_2S\text{-}NR_2$ unit [2]. Many of these organosulfur compounds are employed in stereo and facial selective synthesis of biologically active reagents like amino acids etc [1, 2]. and also in coordination chemistry [3]. Compounds with S-N bonds are of special interest due to the possibilities of sulfur possessing different oxidation states. Also, S-N bond polarization is much different from that of S-O bond, provides necessary flexibility to the systems and for their biological applications. Sulfenamides, ($RS\text{-}NH_2$) 1 are compounds containing trivalent nitrogen are of importance in the synthesis of chiral amines [4]. Stereo chemical interest in sulfenamides arises from the fact that the S-N bond is a chiral axis. The chiroptical properties of sulfenamides are of special interest to physical organic chemist [5, 6]. Kost *et al*. [7] have recently isolated the first stereo stable sulfenamide and demonstrated its chirality by enantiomeric resolution and measurement of cyclic dichroism spectra. Sulfenamides are shown to have applications in many industrial processes including rubber vulcanization, rocket fuels, pesticides pharmaceuticals etc [8-10].

Sulfinamides, ($R(O)\ S\text{-}NH_2$) 2 are important chiral building blocks in organic synthesis. Though these compounds have been known for long time, there is renewed interest in this class of compounds owing to the recognition of their applications in the asymmetric synthesis of many biologically important molecules. Picker gill *et al*. [11] have reported that the alkylated sulfinamides (aminosulfoxonium salts) are used as electrophiles for the formation of C-C bonds, when reacted with β-ketoester enolates. Sulfinamides along with sulfonamides have also been incorporated into peptides and investigated as transition mimics for amide hydrolysis, with potential applicated as peptidase inhibitors [12]. N-acyl derivatives are useful as dual chiral auxiliaries and in the asymmetric enolate alkylation reactions [13].

Sulfonamide, ($R(O)_2S\text{-}NH_2$) 3 and its derivatives are important biologically active compounds including antibacterial, sweeteners and herbicides etc. due to the presence of O_2SNR moiety in these molecules [14]. Several sulfonamides like sulfanilamide, sulfamethiazine, sulfoxazole etc. are employed as antimicrobial chemotherapeutic agents. More than thirty drugs containing this

moiety are in clinical use [15]. The sulfonamide group is strongly electron attracting, leading to a high electron density on the sulfone oxygen atoms and enhancing the acidity of proton attached to nitrogen [14] N-unsubstituted or monosubstituted sulfonamides behave as acids and readily form salts. In this, research paper we have explored the electronic structure of 1-3 using ab initio MO and density functional methods, with the aim of estimating the variation in the S-N bond strength upon S-oxidation. A comparative study has been carried out between oxidized sufenamide on the basis of bond length, rotational barrier, inversion barrier and negative hyper conjugation.

Methods of Calculation

Ab initio MO [16] and Density Functional (DFT) [17] calculations have been carried out using the GAUSSIAN98W [18] package, Complete optimizations were performed on 1, 2 and 3 their rotational barriers, and corresponding transition states using the B3LYP/6-31+G* [19] and MP2(full)/6-31+G* [20] basis set. Since these molecules possess several lone pairs of electrons, inclusion of diffuse functions in the basis set are important [16]. To study the effect of electron correlation on the geometries and energies, full optimizations have been performed using MP2(full)/6-31+G*, [20] and B3LYP/6-31+G*, [19] levels also. All the minima are characterized by zero point frequencies and S-N rotational transition states are characterized by one negative frequency. Atomic charges in all the structures were obtained using the Natural Population Analysis (NPA) method within the Natural Bond Orbital approach using B3LYP/6-31+G* wave function.

Results and Discussion

Sulfenamides, ($RS-NH_2$) 1 show chiroptical Properties [5, 6]. The S-N rotational barrier in sulfenamides is found to be in the range of 12-22 kcal/mol [5, 21]. The barrier to torsion of S-N single bond has been argued to be mainly due to five factors [22], (1) The four electron interactions (lone pair-lone pair repulsions), (2) the two electron interactions (anomeric interactions), (3) steric factors (arising from the bulkiness of the substituents), (4) the electrosteric effects (arising from the substituents on the phenyl group attached to the sulfur atom), (5) the dπ-pπ interactions. Reed and Schleyer showed that sulfenamides show very strong negative hyper conjugation and dπ-pπ interactions are negligible [23].

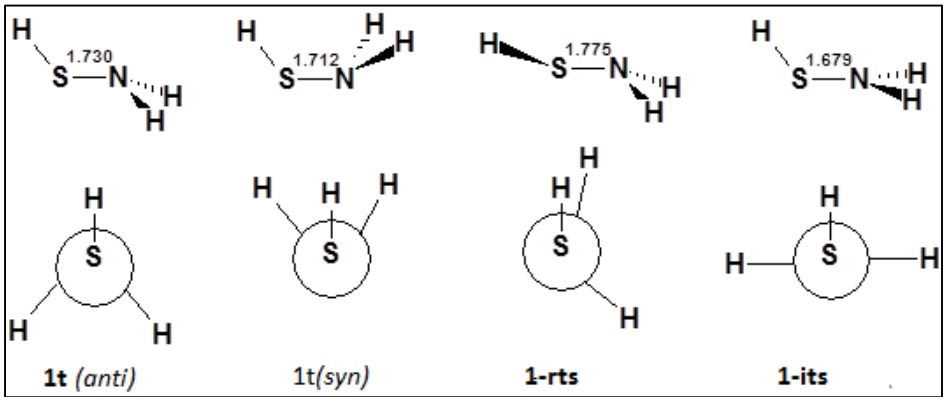

Fig 1: The important geometrical parameters (in Å), structures and Newmann formulas of 1t, 1c, 1-*rts* and 1-*its* at MP2(full)/6-31+G* level.

Theoretical studies on the conformations of sulfenamides was studied using high level *ab initio* calculations and density functional calculations show that sulfenamide has two ground states, 1t (*anti*) and 1c (*syn*) and one rotational transition state, 1-*rts* and one inversion transition state, 1-*its* (Fig.1). The S-N bond length in 1t is 1.730 Å and N-S-H bond angle is 96.5º

(Table 1), but in 1c S-N bond length decreases and N-S-H bond angle increases. In 1-*rts* S-N bond length increases and N-S-H bond angle decreases. The sum of angles around nitrogen (330.6º) in 1t indicates the pyramidal arrangement of nitrogen whereas in 1-*rts* pyramidal character increases (sum of angles is 320.5º). In 1-*its* the S-N bond length is shorter by ~ 0.05 Å relative to 1t and having planar arrangement around nitrogen (sum of angles = 360.0º). These variations in S-N bond length during rotation and inversion attributed to the variation in $n_N \rightarrow \sigma^*_{S-H}$ negative hyper conjugation. Conformation 1t is more stable than 1c by 0.88 kcal/mol. The S-N rotational barrier and N-inversion barrier are 8.09 kcal/mol and 2.04 kcal/mol respectively at MP2(full)/6-31+G* level. The rotational barrier is less than that of experimentally reported torsional barrier 12-22 kcal/mol for the substituted sulfenamides. The high rotational barrier in the experimentally known molecules can be attributed to the steric and electronic factors of the substituent groups. The smaller inversion barrier can be attributed to the increased anomeric effect. The results indicate that d-orbital participation is important in describing the wave function, however the d-p π interactions are absent in sulfenamides. The NBO analysis showed clearly that a strong $n_N \rightarrow \sigma^*_{S-H}$ ($E^{(2)}$ = 4.60 kcal/mol) negative hyper conjugative interactions are present in these systems and it gives partial π character to the S-N interactions. In fact, Schleyer *et al*. have pointed out that sulfenamides are the systems with maximum negative hyper conjugative interactions [23] and this interaction is absent in rotational transition state i.e in the rotational transition state the π bond is broken and the loss of this π character and increased lone pair- lone pair repulsions are responsible for the calculated S-N barrier.

Table 1: The important geometrical parameters, absolute energies, relative energies and second order delocalization energies of the conformers of sulfenamide at MP2(full)/6-31+G* level.

Parameters	1t (*anti*)	1c (*syn*)	1-*rts*	1-*its*
S-N bond length[a]	1.730	1.712	1.775	1.679
H-S-N bond angle[b]	96.5	102.2	96.4	100.9
φ[c]	330.6	338.0	320.5	360.0
Absolute Energy[d]	-453.983706	-453.982175	-453.969890	-453.979096
Relative Energy[e]	0.00	0.88	8.09	2.04
$\underline{n_N \rightarrow \sigma^*_{S-H}}$				
$E^{(2)}$ [f]	4.60	8.09	-	10.3
$\in_J - \in_i$[g]	0.97	0.93	-	0.86
F_{ij}[h]	0.06	0.08	-	0.08

[a] in Å, [b] in degrees, [c] sum of angles around nitrogen, [d] in angstroms units (a. u.), [e] in kcal/mol, [f] second order delocalization energy in kcal/mol, [g] energy difference between the lone pair and antibonding orbitals, [h] overlap matrix.

Sulfinamide

On the potential energy surface of sulfinamide, ($H(O)SNH_2$), 2 two minima, 2a and 2b, two rotational transition states, 2-rts1 and 2-rts2, and one inversion transition state, 2-its were located at HF/6-31+G* level. At HF/6-31G*, MP2/6-31+G*, MP2(full)/6-31+G*, B3LYP/6-31+G* and B3PW91/6-31+G* levels only one minimum. 2a and two rotational transition states, 2-rts1 and 2-rts2 have been found. Because of the small inversion barrier, 2b gets converted into 2a through inversion process at these levels. The geometrical data corresponding to these structures is given in Table 2. The S-N bond length in 2a is 1.677 Å at HF/6-31+G* level, is only slightly longer than that in the X-ray crystal structure of 2, 2, 6, 6-tetradimethyl-4-oxopiperidine (1.652 Å) [24, 25] (In 2, 2, 6, 6-tetramethyl-4-oxopiperidine (A) [24] also N-pyramidalisation is negligible. Hence it is more appropriate to compare the S-N distance in A (1.652 Å) with that in 2-its (1.654 Å) at HF/6-

31+G* level which are in excellent agreement. This supports that the HF/6-31+G* estimates of S-N bond lengths are highly reliable. This distance increases to 1.708 Å and 1.728 Å after including the electron correlation at MP2 and B3LYP levels respectively. The S-N bond length in 2a (1.677 Å) is shorter than S-N single bond length of 1.709 Å in sulfenamide, ($HS-NH_2$), but longer than S=N double bond length (1.537 Å) in S=NH obtained at HF/6-31+G* level, similar trend is observed at MP2 and B3LYP levels also. This leads to the conclusion that there is partial double bond character in sulfinamides. The shorter S-N bond length has been attributed to N lone pair delocalization into the sulfur d-orbital. The smaller S-N distance may be attributed to $n_N \rightarrow \sigma^*_{S-H}$, $n_N \rightarrow \sigma^*_{S-O}$ negative hyper conjugative interactions or S-N electrostatic interactions. The N-S-H angle in 2a is 92.2° at HF/6-31+G* level, small as expected for divalent sulfur. The NH_2 group is highly pyramidalized as indicated by the sum of angles around nitrogen, 333.3° and 332.5° at the HF/6-31+G* and MP2(full)/6-31+G* respectively. In the rotational transition states, 2-rts1 and 2-rts2, the S-N bond length is elongated by ~ 0.03 Å at HF/6-31+G* level. In 2-rts1 and 2-rts2 pyramidal character has increased as expected, sum of angles around nitrogen is 332.6° and 330.6° respectively at HF/6-31+G* level. The lowest energy structure 2a has a conformation in which the lone pair on nitrogen is *anti* to the S-O bond, the lone pairs on sulfur and nitrogen are *gauche* to each other (Fig. 2). This arrangement is ideal for strong $n_N \rightarrow \sigma^*_{S-O}$ anomeric interaction, this second order interaction amounts to 12.41 kcal/mol. In 2b the lone pair on nitrogen is *gauche* with respect to both S- O bond and S lone pairs such that the arrangement leads to $n_N \rightarrow \sigma^*_{S-H}$ interaction. In both 2a and 2b, the Lone pair on S is gauche with respect to lone pair on N. Hence, the instability of 2b can be attributed to the repulsion between the lone pairs on oxygen and nitrogen. The S-N rotational process goes through the transition states, 2-rts1 and 2-rts2, with 2-rts2 having relatively higher energy at all the levels. 2-rts2 has eclipsed arrangement of the lone pairs on S and N, 2-rts1 has *gauche* arrangement of lone pairs on N with respect to that of S-O bond. The S-N rotational path in 2a (via 2-rts2) goes through an energy barrier of 7.6 anomeric delocalisation energy is 1.10 kcal/mol in 2a is weak. The $n_N \rightarrow \sigma^*_{S-O}$ anomeric delocalisation is much stronger (12.41 kcal/mol), but upon rotation this value gets reduced to 1.48 and 1.55 kcal/mol in 2-rts1 and 2-rts2 respectively. This shows that the stabilization of 2a is mainly due to the strong $n_N \rightarrow \sigma^*_{S-O}$ delocalisation and this anomeric interaction causes S-N partial double bond character. In 2a, the $n_O \rightarrow \sigma^*_{S-N}$ donation is also very strong ($E^{(2)}$: 33.89 kcal/mol), which reduces only slightly upon S-N rotation in kcal/mol at the HF/6-31+G*(+ZPE) level. The N-inversion barrier in 2a is 4.9 kcal/mol at HF/6-31+G* level. The energy barrier for the inversion in 2b is only 0.06 kcal/ mol. After including the ZPE correction even this small barrier disappears. At other theoretical levels, 2b and hence 2-its could not be located presumably due to the negligible inversion barrier. The NBO analysis (Table 2) shows that the $n_N \rightarrow \sigma^*_{S-H}$ anomeric delocalisation energy is 1.10 kcal/mol in 2a is weak. The $n_N \rightarrow \sigma^*_{S-O}$ anomeric delocalisation is much stronger (12.41 kcal/mol), but upon rotation this value gets reduced to 1.48 and 1.55 kcal/mol in 2-rts1 and 2-rts2 respectively. This shows that the stabilization of 2a is mainly due to the strong $n_N \rightarrow \sigma^*_{S-O}$ delocalisation and this anomeric interaction causes S-N partial double bond character. In 2a, the $n_O \rightarrow \sigma^*_{S-N}$ donation is also very strong ($E^{(2)}$: 33.89 kcal/mol), which reduces only slightly upon rotation in 2-rts1 ($E^{(2)}$: 30.48 kcal/mol) and 2- rts2 ($E^{(2)}$: 29.14 kcal/mol). $n_N \rightarrow \sigma^*_{S-O}$ 2-rts1 ($E^{(2)}$: 30.48 kcal/mol) and 2- rts2 ($E^{(2)}$: 29.14 kcal/mol). $n_N \rightarrow \sigma^*_{S-O}$ interaction induces small π character between S and N whereas $n_O \rightarrow \sigma^*_{S-N}$ interaction reduces the σ character, these two factors oppose each other and hence the S-N bond order is not strongly effected.

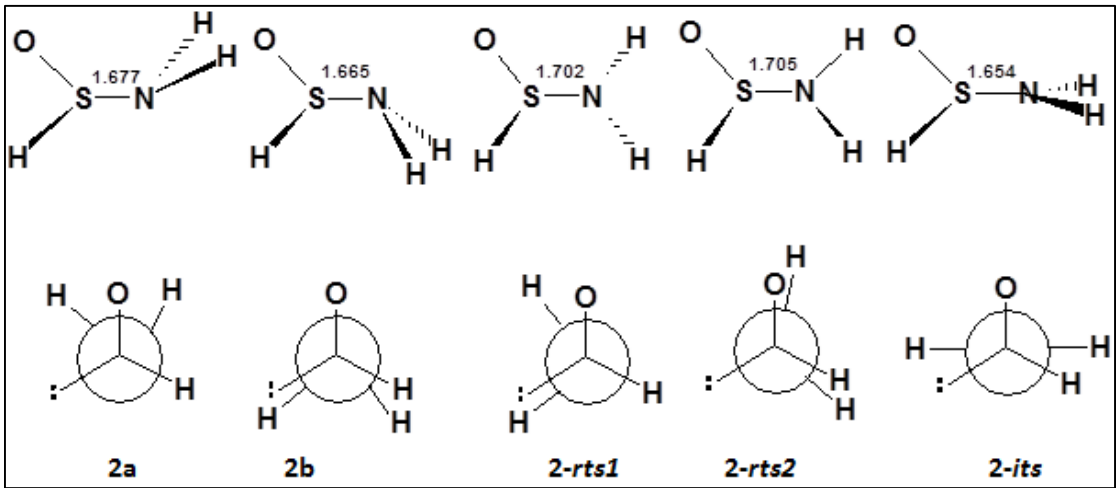

Fig 2: The geometrical parameters (in Å), structures and Newmann projections of 2a, 2b, 2-*rts1*, 2-rts2 and 2-*its* at MP2(full)/6-31+G* level

Table 2: The important geometrical parameters, relative energies and second order delocalization energies of the conformers of sulfinamide at MP2(full)/6-31+G* and HF/6-31*G* (in Parenthesis) level.

Parameters	**2 a**	**2b**	**2-*rts1***	**2-*rts2***	**1-*its***
S-N bond length[a]	1.708 (1.677)	--- (1.665)	1.743 (1.702)	1.740 (1.705)	--- (1.654)
H-S-Nbond angle[b]	89.3 (92.2)	--- (98.1)	90.0 (91.0)	94.8 (95.6)	--- (97.2)
φ[c]	332.8 (333.3)	--- (347.0)	331.2 (332.6)	357.9 (330.6)	--- (354.8)
Relative Energy[d]	0.00	--- (4.8)	8.2 (8.0)	9.4 (8.4)	--- (4.9)
$\underline{n_N \rightarrow \sigma^*_{S-H}}$					
$E^{(2)}$ [e]	1.10	---	1.85	2.72	---
$\underline{n_N \rightarrow \sigma^*_{S-O}}$					
$E^{(2)}$ [e]	12.41	---	1.48	1.55	---
$\underline{n_O \rightarrow \sigma^*_{S-N}}$					
$E^{(2)}$	33.89	---	30.48	29.14	---

[a] in Å, [b] in degrees, [c] sum of angles around nitrogen, [d] in kcal/mol, [e] second order delocalisation energy in kcal/mol

Sulfonamide

On the potential energy surface of sulfonamide, ($H(O)_2SNH_2$) 3, two minima, 3a and 3b, one rotational transition state, 3-rts and one 0inversion transition state, 3-its were located (Fig. 3). Both Ground state structures, 3a and 3b are found to have C_s symmetry, the basic difference between the two structures is arising from the arrangement of -NH_2 group *syn* (3a) or *anti* (3b) with respect to the SO_2 group. The topomerisation between the two structures 3a and 3b is probable either through rotation around S-N or through inversion at nitrogen. The S-N bond length in 3a is 1.636 Å at HF/6-31+G* level. After including electron correlation at MP2 and B3LYP levels the bond length elongates to 1.667 Å and 1.682 Å respectively. The S-N bond distance in 2a (1.667 Å) is shorter than S-N single bond distance of 1.733 Å calculated for sulfenamide but longer than S=N double bond distance (1.596 Å) in HN=S both obtained at MP2/6-31+G* level, similar trend is observed at HF and B3LYP levels also. This reduction in the S-N distance may be attributed to (a) partial double bond character due to $n_N \rightarrow \sigma^*_{S-H}$ anomeric π interactions as in sulfonamides. The arrangement of atoms.

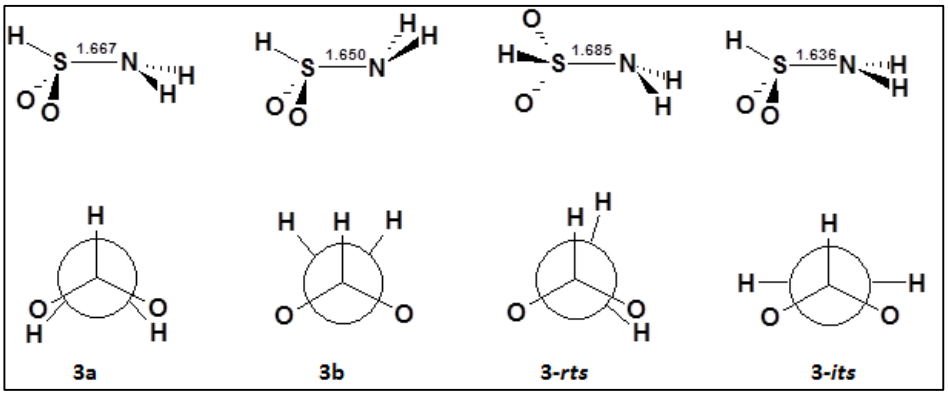

Fig 3: The geometrical parameters (in Å), structures and the Newmann formulas of 3a, 3b, 3-*rts* and 3-***its*** at MP2/6-31+G* level

Table 3: The important geometrical parameters, relative energies and second order delocalisation energies of the conformers of sulfonamide at MP2/6-31+G* level.

Parameters	**3a**	**3b**	**3**-*rts*	**3**-*its*
S-N bond length[a]	1.667	1.650	1.685	1.636
H-S-N bond angle[b]	100.5	98.5	105.3	104.5
Relative Energy[c]	0.00	1.40	7.63	1.20
φ[d]	336.7	339.7	--	--
$\underline{n_N \rightarrow \sigma^*_{S\text{-}H}}$				
$E^{(2)}$ [e]	5.86	10.78	0.71	11.66
$\underline{n_O \rightarrow \sigma^*_{S\text{-}N}}$				
$E^{(2)}$ [e]	16.48	24.61	14.62	14.59
$\underline{n_N \rightarrow \sigma^*_{S\text{-}O}}$				
$E^{(2)}$ [e]	3.23	2.73	5.83	3.60
$\underline{n_O \rightarrow \sigma^*_{S\text{-}H}}$				
$E^{(2)}$ [e]	22.01	22.61	23.25	22.65

[a] in Å, [b] in degrees, [c] in kcal/mol, [d] sum of angles around nitrogen, [e] second order delocalisation energy in kcal/mol.

Around N (1) shows pyramidal character [26] with sum of angles around N (1) being 336.7°. The strong pyramidalisation at nitrogen indicates weak anomeric S-N interaction. The S-N bond length in 3b is 1.650 Å (Table 3) at MP2/6-31+G* level which is smaller as compared to that in conformation 3a by 0.017 Å. The decrease in S-N bond distance is accompanied by increase in S-H bond distance (0.005 Å), and increase in N1-S2-H3 angle (3.6°), decrease in N pyramidalisation (sum of angles around nitrogen 339.7°) and increase in $n_N \rightarrow \sigma^*_{S\text{-}H}$ interaction energy suggesting an increase in the negative hyper conjugation [26]. The S-N bond length in 3-rts is 1.685Å (increases by 0.018 Å relative to 3a). However, in 3-rts the repulsions between lone pairs on nitrogen and oxygen's are stronger, which destabilizes the structure. These two opposing factors influence the S-N rotational path. The inversion transition structure 3-its has S-N bond distance of 1.636 Å (decreases by 0.031 Å relative to 3a) at MP2/6-31+G* level. The S2-H3 bond distance increases by 0.004 Å and the bond angle N1-S2-H3 increases by 4.0°. The relative energy of the conformation 3b is 1.40 kcal/mol higher as compared to 3a at HF/6-31G* level. The ΔE between 3a and 3b gets reduced with the increase in the complexity of the quantum mechanical level. Conformer 3a has eclipsed arrangement and 3b has staggered arrangement, hence 3b is expected to have lower

energy. The lower energy for 3b is also expected because of the stronger $n_N \rightarrow \sigma^*_{S-H}$ hyper conjugation in 3b compared to that in 3a. This indicates that the repulsions between the lone pairs of electrons on N and O are very strong in 3b (stronger than the destabilization in 3a due to eclipsing and the extra stabilization due to stronger anomeric effect in 3b) and make it relatively unstable. The S-N rotation barrier in 3a at MP2/6-31+G* level is 7.63 kcal/mol. Negative hyper conjugative ($n_N \rightarrow \sigma^*_{S-H}$) interaction is not responsible for the high rotational barrier in sulfonamides because both 3a, 3-rts have anomeric interactions. The N-inversion barrier in 3a is 1.20 kcal/mol at MP2/6-31+G*. Natural bond orbital (NBO) analysis has shown that the second order energy energies for the $n_N \rightarrow \sigma^*_{S-H}$ (5.86 kcal/mol) and $n_N \rightarrow \sigma^*_{S-O}$ (3.23 kcal/mol) interactions are weaker than the $n_O \rightarrow \sigma^*_{S-H}$ (22.01 kcal/mol), $n_O \rightarrow \sigma^*_{S-O}$ (30.04 kcal/mol) and $n_O \rightarrow \sigma^*_{S-N}$ (16.48 kcal/mol) interactions. In 3a the anomeric π_{S-N} strength gained through the $n_N \rightarrow \sigma^*_{S-H}$ (or σ^*_{S-O}) gets nullified due to the $n_O \rightarrow \sigma^*_{S-N}$ interactions. This indicates that the $n_N \rightarrow \sigma^*_{S-H}$ anomeric interaction in 3a is stronger, but this does not increase the S-N bond order because of the $n_O \rightarrow \sigma^*_{S-N}$ interactions. The kind of three-dimensional negative hyperconjugation present in 3a seems to provide additional strength to S-N and S-O bonds. Because of this extra strength, the S-N bond cleavage becomes difficult in sulfonamides. In the rotational transition state 3-rts, the lone pair of nitrogen is in plane with one of the S-O bonds. The $n_N \rightarrow \sigma^*_{S-O}$ interaction is stronger than the $n_N \rightarrow \sigma^*_{S-H}$ interaction and hence stronger anomeric stabilization is expected in 3-rts compared to 3a and 3b. For example, the S-N distance in 3-rts increases only by 0.016 Å during rotation. In the inversion transition state 3-its, $E^{(2)}$ for the $n_N \rightarrow \sigma^*_{S-H}$ delocalisation increases by 6.80 kcal/mol relative to 3a. This indicates stronger negative hyperconjugation in 3-its compared to that in 3a. It is also reflected by low inversion barriers.

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Conclusions

Ab initio MO and Density Functional (DFT) calculations on 1, 2 and 3 at different levels showed that the changes observed in S-N bond lengths, S-N rotational barrier indicate that S-N bond is very weak in these systems. The weakness observed in S-N bond originates from the negative hyperconjugation in these systems.

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