ISSN: 2321-4902
Volume 1 Issue 4

Online Available at www.chemijournal.com

International Journal of Chemical Studies

Electronic structure of $R(O)_nSN=CH_2$ (n=0,1,2) systems

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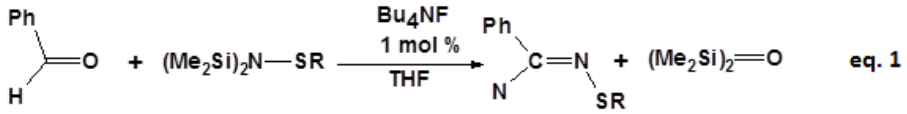
Ab initio calculations have been performed on $R(O)_nSN=CH_2$ (n=0,1,2) systems. Complete optimizations using HF/6-31+G*, MP2(full)/6-31+G* and B3LYP/6-31+G* levels show that sulfenimine (1), sulfinimine (2) and sulfonimine (3) prefer to have *synperiplanar* arrangement. NBO analysis has been carried out to quantitatively estimate these delocalisations.

Keyword: Ab initio, NBO analysis, sulfenimine, sulfinimine, sulfonimine

Introduction

$R(O)_nSN=CH_2$ (n=0,1,2) are important species belonging to the general class of N-sulfur binding imines. Sulfenimines, ($RS-N=CH_2$) 1 (also known as N-sulfenylimine and N-alkylidenesulfenamide) have been used as intermediates in the synthesis of cephalosporin, cephamycines and carbohydrate derivatives [1]. Sulfenimines can be prepared from sulfenamides, disulfides, sufenyl halides and sufenamide enolate equivalents. Morimoto reported a convenient general synthesis of sulfenylimines by the reaction of aldehydes and ketones with N, N-bis(trimethylsilyl) sulfenamides in the presence of tetrabutylammonium fluoride catalyst (eq. 1) [2].



eq. 1

The interactions between sulfur and nitrogen in these systems is a topic of special interest. On one hand we may expect a partial pπ-pπ bond between sulfur and nitrogen because isoelectronic *S*-nitrosothiols show *cis-trans* isomerisation across this bond [3]. On the other hand anomeric π bond due to $n_N \rightarrow \sigma^*_{S-R}$ negative hyper conjugation should be expected as in sulfonamides [4a]. These two interactions are in orthogonal planes and could be playing important role. Davis and coworkers [5] estimated planar N-inversion barrier in N-sulfenylimines and reported that they are smaller than the N-inversion barrier in imine. The low N-inversion barriers have been attributed to the d-orbital participation on sulfur, but our studies on the S-N interactions in sulfenamides [4a] sulfonamides [4b] and sulfinimines [4c, d] indicate negligible participation from the d-orbitals on sulfur. Hence, it is important to study the reasons for the relatively lower N-inversion barriers in N-sulfenylimines.

Sulfinimine, ($R(O)S-N=CH_2$) 2 (thiooxime S-oxide, N-alkylidenesulfinamide) [6] are of current interest with the recognition of their ability to stereo selectively produce amines [7]. and their applications in the preparation of amino acids. Sulfinimines show exceptional facial selectivity apart from reactions with nucleophiles [9]. Sulfinimines are also found to be an excellent

route for the preparation of asymmetric aziridines [8]. which in turn are important starting materials for the preparation of alkaloids, amino acids and β-lactam, antibiotics etc. The N-sulfinyl auxiliary (S(:)(O)R group) in sulfinimines increases the electrophilicity of N=C unit and also prevents the competitive enolisation of this unit [9]. The dπ-pπ bonding between sulfur and the –N=CR_2 had been expected to be the origin of this increased electrophilicity [10]. Davis *et al* have suggested that the conjugation between C=N bond and the S=O bond through the S-N bond is absent in sulfinimines, but localised pπ-dπ interactions between nitrogen and sulfur are responsible for the transfer of electronic effects through the S-N bond [10].

Reed and Schleyer [11] have shown that in S-N interactions of sulfenamides and in hypervalent sulfur compounds, the orbital participation should not be invoked and the observed high barrier is due to negative hyperconjugation. The C-N-S-O unit in sulfinimine is often represented as if it has a *synperiplanar* (*s-cis*) arrangement. The stereo and facial selectivities observed in the reactions of sulfinimines have been explained assuming *synperiplanar* arrangement [7, 8]. The origin of this preference can be attributed to (1) the repulsions among the lone pairs of electrons present on N, S and O atoms, (2) the $n_N \rightarrow \sigma^*_{S-O}$ negative hyperconjugation and (3) the intramolecular C-H----O electrostatic interactions. The semirigidity of C-N-S-O unit is responsible for the stereoselectivity and facial selectivity of sulfinimines.

Sulfonimines, ($R(O)_2S$-N=CH_2) 3 (N-sulfonylimines, N-alkylidenesulfonamide) have been the centre of attraction for organic chemists because of their ability as synthetic reagents [12]. Weinreb *et al* have shown that sulfonimines are of importance because they are one of the few types of electron deficient imines that are stable enough to be isolated but reactive enough to undergo addition reactions [13]. These can be prepared by the oxidation of sulfenimine [14]. These have been exploited for their electron deficient imine bond. For example, Boger and coworkers have described the inverse electron demand Diels-Alder chemistry of N-sulfonyl α,β-unsaturated imines for the implementation of the 4π participation of 1-aza-1,3-butadienes in Diels-Alder reactions [15]. Supuran and coworkers [16]. Studied the sulfonylguanidine, and its derivatives for their thrombin inhibitor activity and found to have moderate but intrinsically selective activity. The presence of SO_2 group in the neighbourhood of guanidine moiety reduces its basicity providing high selectivity. Because of the biological importance the study of rotation around different bonds is essential to understand the feasible arrangement necessary for the facile reactions and we have studied the same for N-sulfonylimines. In this paper electronic structure of 1, 2, and 3 has been studied using a*b initio* MO[17] and Density Functional (DFT) [18] calculations and a comparison is made between their bond lengths, rotational barrier and inversion barrier upon S-oxidation.

Methods of Calculation

Ab initio MO [17] and Density Functional (DFT) [18] calculations have been carried out using the GAUSSIAN98W [19] package, Complete optimizations were performed on 1, 2 and 3 their rotational barriers and corresponding transition states using the B3LYP/6-31+G* [18] 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 [18]. To study the effect of electron correlation on the geometries and energies, full optimizations have been performed using MP2(full)/6-31+G* and B3LYP/6-31+G* 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.

Results and Discussion

Elctronic Structure of Sulfenimine

The complete optimization of different conformations of HSN=CH_2, 1, indicated the presence of two minima, 1c and 1t and one

rotational transition state, 1-*rts* and N-inversion transition state, 1-*its* (Fig. 1) on the potential energy surface. The S-N and C=N bond lengths are given in Fig. 1 obtained at HF/6-31+G*, MP2(full)/6-31+G* and B3LYP/6-31+G* levels. Both the ground state structures, 1c and 1t are found to have C_s symmetry. The S-N bond length in 1c is 1.688 Å at HF/6-31+G* level, this distance increases to 1.702 Å after including the electron correlation at MP2 and B3LYP levels. The C=N bond length in 1c is 1.284 Å which is comparable to that in H_2C=NH (1.283 Å) at MP2(full)/6-31+G* level. The S-N bond length in 1c is shorter than that (1.712 Å) in sulfonamide [4c], suggesting that there is a partial π bond between sulfur and nitrogen in 1c. The S-N bond length in 1t is longer than that in 1c at all the levels. For example, at the MP2(full)/6-31+G* level, the S-N bond length is longer in 1t by 0.026 Å. The N-S-H angle in 1c and 1t is 100.3° and 94.2° respectively at MP2(full)/6-31+G* level, close to that of divalent sulfur. The shorter S-N bond length and longer N-S-H bond angle in 1c relative to 1t suggest that there is strong negative hyperconjugative interaction in 1c, because similar trend was observed between 1c and 1t of sulfonamide due to negative hyperconjugation [40]. In the S-N bond rotational transition state, 1-rts the S-N bond length is 1.774 Å at MP2(full)/6-31+G* level, an elongation by 0.072 Å with respect to 1c. In the N-inversion transition state, 1-its, the S-N bond length is 1.587 Å, a contraction by 0.115 Å with respect to 1c at the same level. The energy difference (ΔE) between the 1c and 1t isomers in 1 is 1.46 kcal/mol at HF/6-31+G* level. The S-N rotational barrier in 1 is 5.15 kcal/mol at HF/6-31+G* (+ZPE) level. Inclusion of electron correlation using Moller-Plesset method increases the rotational barrier by 0.76 kcal/mol, but

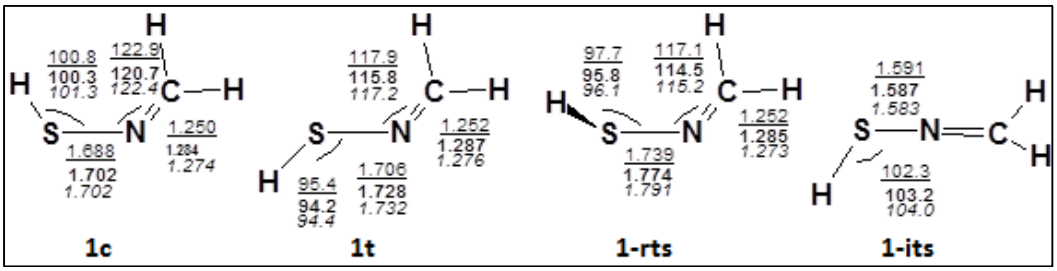


Fig 1: The structures and the geometrical parameters of different conformers of N-sulfenimines obtained by using HF, MP2(full) and *B3LYP* levels using 6-31+G* basis set (bond lengths in Å and angles in degrees).

the inclusion of electron correlation using density functional B3LYP method increases the barrier by 1.09 kcal/mol. The S-N rotational barrier in 1 (5.91 kcal/mol) is less as compared to sulfenamide, (8.09 kcal/mol at MP2(full)/6-31+G* level). The smaller rotational barrier in 1 as compared to sulfenamide may be due to weaker negative hyperconjugative interactions in 1. NBO analysis in 1c showed that second order energy ($E^{(2)}$) associated with the $n_N \rightarrow \sigma^*_{S-H}$ delocalisation (anomeric π interactions) is 5.56 kcal/mol. In 1t this negative hyperconjugative interaction becomes very weak ($E^{(2)}$: 1.69 kcal/mol) and in 1-*rts* it becomes negligible. Because of the weaker negative hyperconjugation, the S-N bond length in 1t is longer than that in 1c. NBO analysis shows a second order delocalisation due to $n_S \rightarrow \pi^*_{C=N}$ interaction in 1c ($E^{(2)}$: 21.87 kcal/mol). This delocalisation induces partial π character between sulfur and nitrogen. Hence it can be concluded that there are two types of partial π bonds between sulfur and nitrogen in N-sulfenylimine. These two are in orthogonal planes i.e. pπ-pπ bond is perpendicular to the molecular plane and anomeric π bond is in the molecular plane. During S-N rotation both these interactions get destroyed, increasing the S-N bond length and are responsible for the rotation barrier. However, the S-N rotational barrier in 1 is weaker than that in sulfenamide, which has only anomeric π character. This analysis suggests that the

combined strength of partial pπ-pπ bond and anomeric π bond in 1c is weak. To verify this observation we have estimated the S- N bond dissociation energy (Table 2.21) in 1c and 1t, which are 56.07, 66.14 kcal/mol respectively. The smaller S-N bond dissociation energy in 1c confirms that the S-N bond strength is weaker compare to that in 1t. The *3p–2p* interaction leading to pπ-pπ bond is weak because of the smaller overlap between the *3p* and *2p* orbitals. The planar N-inversion barrier in 1 is 25.26 kcal/mol MP2(full)/6-31+G* level. This value is comparable to the experimental estimation of planar N-inversion barrier (20.3 – 20.8 kcal/mol) in arylsulfenimines, $XC_6H_4SN=CMe_2$ (X = H, 4-Cl, 4-Br, 3-NO_2, 4-NO_2) [21]. These values are lower than that in imine CH_2=NR (~ 30 – 32 kcal/mol).

Table 1: Absolute Energy, Relative Energy. second order delocalisations and bond dissociation energy of sulfenimines, $RSN=CH_2$ at MP2(full)/6-31+G* level.

Parameters	1c	1t	1-rts	1its
A E[a]	-491.9586930	-491.9610768	-491.9509411	-491.9208155
R E[b]	0.00	1.49 (1.41)	6.36 (5.91)	25.26 (24.62)
$\underline{n_S \rightarrow \sigma^*_{S-H}}$ E (2) c	5.86	1.69	---	17.95
$\underline{n_S \rightarrow \sigma^*_{C=N}}$				
E (2) c	4.18	0.06	---	11.15
$\underline{n_s \rightarrow \pi^*_{C=N}}$	21.87	18.57	---	43.75
E (2) c				
B D E[d]	56.07	66.14	--	--

[a] Absolute energy in Å, [b] relative energy in kcal/mol, [c] second order energy in kcal/mol, [d] bond dissociation energy in kcal/mol.

Davis *et al*. [21b] have rationalized this observation in terms of the donation of electrons from nitrogen to the d-orbital on sulfur. In the two ground states 1c, 1t and during the S-N bond rotation (i.e. in 1-*rts* the d-orbital participation has been found to be negligible. However, in the inversion transition state 1-*its*, the d-orbital occupancy significantly increased. Infact the $n_S \rightarrow \sigma^*_{C=N)}$ delocalisation in 1-*its* amounts to 11.15 kcal/mol and $n_N \rightarrow \sigma^*_{S-H}$ delocalisation amounts to 17.95 kcal/mol (much larger than that in 1t) (Table 1). Hence, it may be concluded that in 1\-*its* the d-orbital participation as well as negative hyperconjugative interactions together play important role. NBO analysis on 1-*its* clearly supports this argument, there is an increase in the second order energy $E^{(2)}$ due to $n_N \rightarrow \sigma^*_{S-H}$ and $n_S \rightarrow \pi^*_{C=N}$ delocalisation (17.95 and 43.75 kcal/mol respectively). The decrease in the S-N and C=N (1.587 and 1.261 Å respectively) bond lengths in 1-*its* is indicative of increase of bond order between the respective atoms. The high inversion barrier seems to be the result of increase in lone pair–lone pair repulsions between sulfur and nitrogen in 1-*its*. The high inversion barrier makes the transformation of 1c to 1t improbable through inversion rather occurs through rotation.

Elctronic Structure of Sulfinimine

Ab initio calculations at HF/6-31+G*, MP2/6-31+G* and B3LYP/6-31+G* levels have shown that there are three minima corresponding to the three rotamers of sulfinimines, 2 (Fig. 2) along the S-N rotational path. The data shows that S-N and S=O bond distances at HF/6-31+G* level are comparable to the experimentally reported crystallographic data. The dihedral angle between the C-N-S and N-S-O planes in **2** is –13.7° at the same level (Table 2), which clearly indicates that the

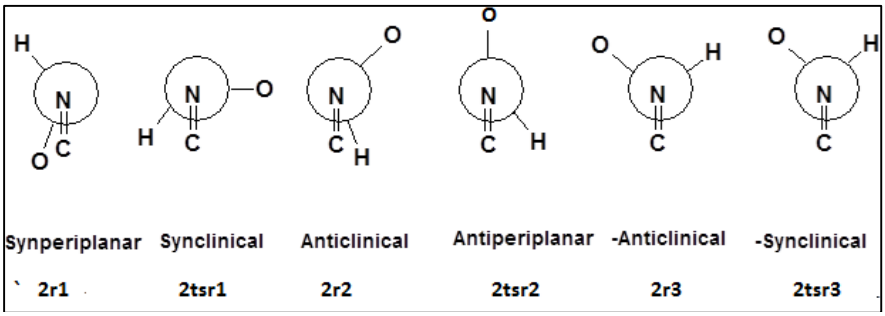


Fig 2: The Newman projection of the various conformers of the sulfinimines

basic C-N-S-O unit in sulfinimines prefers an almost planar arrangement, close to a *synperiplanar* conformation. The small torsional angles of 2 are comparable to the reported crystal structure, which is shown to have *s-cis* arrangement. S-N, C=N and S-O bond lengths show that there is no π conjugation in sulfinimines and hence preference for *s-cis* arrangement is not due to π conjugation. The origin of semirigid *synperiplanar* arrangement can be attributed to (i) the repulsions between the lone pairs of electrons on nitrogen, sulfur and oxygen and (ii) the $n_N \rightarrow \sigma^*_{S\text{-}O}$ negative hyperconjugation. The semirigidity of C-N-S-O unit is responsible for the stereo selectivity and facial selectivity of sulfinimines. The S-N rotational barrier is higher than the S-N single bond in sulfenamides[4c]. In 2, the σ* orbital of S-O bond has the proper arrangement such that it can accept electron density from the lone pair of nitrogen. Hence, it is possible for the molecule to possess $n_N \rightarrow \sigma^*_{S\text{-}O}$ negative hyper conjugation. During rotation the S-N bond length increases by 0.014 Å, this is due to the loss of $n_N \rightarrow \sigma^*_{S\text{-}O}$ negative hyper conjugation. Thus the high rotational barrier is due to the loss of $n_N \rightarrow \sigma^*_{S\text{-}O}$ negative hyper conjugative interaction during rotation and intramolecular H-bonding. Atomic charges calculations have shown that the S-O bond is strongly polar. The sulfinyl group in sulfinimines polarizes the C=N bond, while withdrawing electron through inductive effect leads to the Michael acceptor character of sulfinimines. The S-N rotational barrier in 2 is 9.73 kcal/mol (very high), while S-N bond dissociation energy is less in 2 (3.20 kcal/mol). The increase in the S-N bond length is due to the presence of pπ-pπ hyper conjugation is small and it leads to the increase in S-N rotational barrier. In 2 intramolecular H-bonding is present that also supports the reason for the increase in S-N rotational barrier

Table 2: The important geometrical parameters, absolute energies and relative energies of sulfinimine, 2 at HF/6-31+G* level.

Parameters	2r1	2tsr1	2r2	2tsr2	2r3	2tsr3
C=N[a]	1.251	1.253	1.251	1.251	1.254	1.255
S-N[a]	1.698	1.712	1.699	1.713	1.719	1.720
S-O[a]	1.473	1.471	1.467	1.463	1.467	1.469
O-N-S[b]	117.1	118.2	120.3	118.5	114.4	114.3
N-S-O[b]	111.1	108.4	108.3	108.2	108.6	108.8
C-N-S-O[b]	-13.7	75.9	111.6	164.4	245.2	256.1
R. E.[c]	0.00	9.20	8.90	9.78	7.20	7.12

[a] in angstroms, [b] in degrees, [c] relative energy in kcal/mol.

Electronic Structure of Sulfonimine

On the S-N rotational path of N-sulfonimines, ($H(O)_2SN=CH_2$) three minima, 3, 3´ and 3-r, and three rotational transition states, 3-rts1, 3-rts2 and -rts2´ could be located. Out of the three minima, two (3 and 3´) are of the same energy because the

two configurations have equivalent stereo chemistry arising from equivalent oxygen atoms with respect to C=N double bond. (Fig. 3 and 4). The arrangement of C=N double bond in 3 and 3´ is *synperiplanar* with respect to two oxygens respectively, while in third minimum (3-r) it is *synperiplanar* to S-H. The 3-r is having C_s symmetry, while 3 and 3´ have C_1 symmetry. The structural data corresponding to these structures obtained at HF/6-31+G*, MP2(full)/6-31+G* and B3LYP/6-31+G* levels are given in Fig. 3. The structures 3, 3´ are more stable relative to 3-r. Three rotational transitions states corresponding to topomerisations from 3 to 3´, 3 to 3-r and 3´ to 3-r are labeled as 3-rts1, 3-rts2 and 3-rts2´ respectively (Fig. 4). The structures 3-rts2 and 3-rts2´ are of same energy. The rotational transition state 3-rts1 has *antiperiplanar* arrangement of C=N double bond with respect to hydrogen and in 3-rts2 it is *antiperiplanar* with respect to oxygen (Fig.4). The S-N bond length in 3 is 1.668Å at HF/6-31+G* level, after including the electron correlation at MP2 and B3LYP levels the bond length elongates to 1.725 Å and 1.738 Å (Fig. 3) respectively. The S-N bond length in3-r is 1.707Å at MP2(full)/6-31+G* level, which is smaller as compared to that in conformation 3 by 0.018 Å.

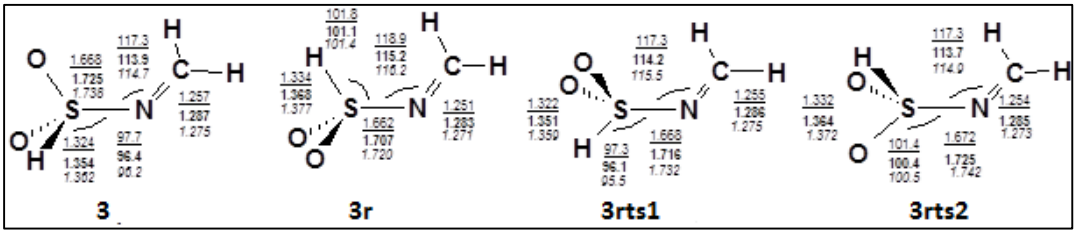


Fig. 3: The structures and the important geometrical parameters of different conformers of sulfonimines obtained by using HF, MP2(full) and *B3LYP* levels using 6-31+G* basis set (bond lengths in Å and angles in degrees).

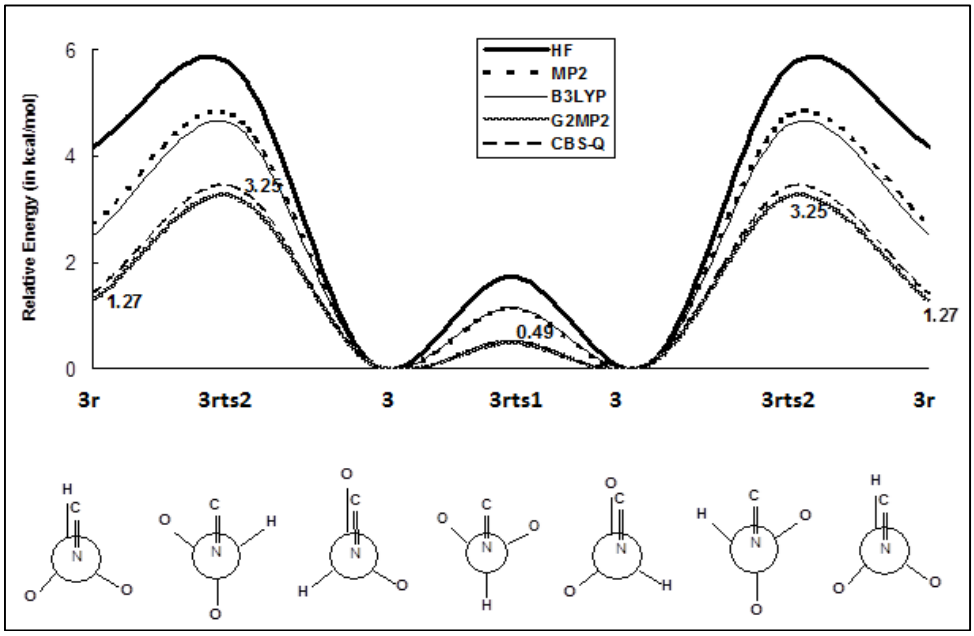


Fig 4: The potential energy surface and Newman projections of the different conformers of sulfonylimine, 3 on its S-Nrotational path.

The C=N bond length in **3** is 1.287Å, which is slightly longer than that in H_2C=NH (1.287 Å) at MP2(full)/6-31+G* level. The energy difference (ΔE) between the two minima (3 and 3-**r**) is 2.71 kcal/mol at MP2(full)/6-31+G*. The S-N rotational barrier observed in 3 is much less than

that observed in other systems (7-22 kcal/mol) [11], and is in the range of C-C single bond rotational barrier in ethane (~ 3 kcal/mol). The minima on the S-N rotational path in 3 have *antiperiplanar* arrangement between the lone pair on nitrogen and the S-X bond (X= O in 3 and 3´ and H in 3-r). This arrangement is favorable for negative hyper conjugative delocalisations of lone pair electrons on nitrogen. However, the minima 3 and 3´ have eclipsing arrangement between N=C and S=O bonds.

Table 3: Absolute Energy, Relative Energy and second order delocalisations sulfonimines, 3 $R(O_2)SN=CH_2$ at MP2(full)/6-31+G* level.

Parameters	3	3r	3-rts1	3-rts2
A E[a]	-642.008916	-642.004596	-642.007110	-642.001298
R E[b]	0.00	2.71	1.13	4.78
$\underline{n_O \rightarrow \sigma^*_{S\text{-}N}}$ E (2) c	35.92	- -	--	--
$\underline{n_O \rightarrow \sigma^*_{S\text{-}H}}$ E (2) c	23.06	--	- -	--
$\underline{n_N \rightarrow \sigma^*_{S\text{-}O}}$ E (2) c	6.74	--	--	--

[a] Absolute energy in Å, [b] relative energy in kcal/mol, [c] second order energy in kcal/mol

hence the overall energy gain is not substantial in 3. The transition states on the S-N rotational path i.e. 3-rts1 and 3-rts2 have *synperiplanar* arrangement between the lone pair of electrons on nitrogen and S-X bond, which is less favorable for negative hyper conjugative delocalisation. Similarly, in 3-rts2 the lone pair on nitrogen is in an unfavorable position with respect to the lone pair on oxygen and thus repulsive interactions cause an increase in the energy of 3-rts2. Hence, it can be concluded that $n_N \rightarrow \sigma^*_{S\text{-}X}$ interactions as well as n_N vs. n_O repulsions complement each other in dictating the conformational preferences of *N*- sulfonylimines. However, since the rotational barrier is small, no preference should be expected at room temperature. NBO analysis shows that the second order energy for $n_O \rightarrow \sigma^*_{S\text{-}N}$ delocalisation ($E^{(2)}$ = 35.92 kcal/mol) is very strong. This interaction increases the S-N bond length in 3. The increased bond length reduces the anomeric π overlap and causes a reduction in the rotational barrier in 3.

Acknowledgements

Author is thankful to Prof. (Dr.) P V Bharatam, Dept. of Medicinal chemistry, NIPER, Mohali and Prof. (Dr.) Damanjit Kaur, Dept. of chemistry, G N D U, Amritsar, for their valuable suggestions.

Conclusions

Ab initio MO and Density Functional (DFT) calculations on 1, 2 and 3 at different levels showed that in 1, S-N bond length is shorter than in 2 due to the absence of negative hyper conjugative interactions, rather pπ - pπ interactions are important in 2. The S-N bond length in 3 is shorter than in 1 indicates stronger negative hyper conjugation in 3 as compared to 1.

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