Theoretical investigation on the conformational preferences of sulfinimines

PERKIN 2

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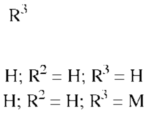
The potential energy surfaces of sulfinimine, $H_2C{=}NS(O)H$, **1**, and methylsulfinimine, $MeHC{=}NS(O)H$, **2**, have been searched, using the *ab initio* MO and Density Functional Methods, to study the conformational preferences. Complete optimizations at HF/6-31G*, HF/6-31+G*, MP2/6-31+G* and B3LYP/6-31+G* levels on **1** showed that there are three minima on the path of rotation around N–S bond in **1**. A conformer with synperiplanar arrangement, with the C–N–S–O torsional angle close to 13°, has been found to be the most preferred. Repulsions between the lone pairs of electrons present on N, S and O atoms are responsible for the observed conformational preferences of **1**. The N–S bond rotational barrier in **1** is 9.16 kcal mol^{-1} at the B3LYP/6-31+G*(+ZPE) level. This high energy barrier can be attributed to the $n_N \longrightarrow \sigma^*_{SO}$ negative hyperconjugation and to the repulsive interactions between the lone pairs of electrons. The planar N-inversion barrier in **2Z** is 18.72 kcal mol^{-1} at the B3LYP/6-31+G* (+ZPE) level, comparable to experimental values.

Introduction

Sulfinimines (thiooxime *S*-oxides, *N*-alkylidenesulfinamides)[1] are important species belonging to the general class of *N*-sulfur binding imines, $R_2C{=}NS(O)_nR$ ($n = 0,1,2$). There is current interest in these compounds[2] with the recognition of their ability stereoselectively to produce amines[3] and their application in the preparation of amino acids.[4] Sulfinimines show exceptional facial selectivity apart from reactions with several nucleophiles.[2–12] Sulfinimines are also found to be excellent intermediates for the preparation of asymmetric aziridines,[6] which in turn are important starting materials for the preparation of alkaloids, amino acids, and β-lactam antibiotics, *etc.* One of the important reactions of aldehyde derived sulfinimines is to produce, on heating, sulfenic acids which are key intermediates in many biological transformations.[7] Recycling of sulfinimines and removal of sulfinyl auxiliaries can readily be carried out under mild reaction conditions.[8] In the recent past sulfinimines have been successfully employed in the synthesis of several types of amino acids,[4,9] α-aminophosphonic acids,[10] the taxol side chains,[11] arylpyrrolines,[12] azomethine ylides,[5a] *etc.*



1: $R^1 = H$; $R^2 = H$; $R^3 = H$
2*E*: $R^1 = H$; $R^2 = H$; $R^3 = Me$
2*Z*: $R^1 = H$; $R^2 = Me$; $R^3 = H$
3: $R^1 = p$-Tolyl; $R^2 = H$; $R^3 =$ Phenyl
4: $R^1 = p$-Tolyl; $R^2 = Me$; $R^3 =$ Phenyl

The *N*-sulfinyl auxiliary, S(:)(O)R group, in sulfinimines increases the electrophilicity of the N=C unit and also prevents competitive enolization of this unit.[2] The dπ–pπ bonding between sulfur and $N{=}CR_2$ had been expected to be the origin of this increased electrophilicity.[13a] Davis *et al.* have suggested that conjugation between the C=N and the S=O bonds through the N–S bond is absent in sulfinimines, but localized p–d π interactions between nitrogen and sulfur are responsible for the transfer of electronic effects through the N–S bond.[13] They also found that the localized p–d π interactions between nitrogen and sulfur are maximum when the nitrogen atom has sp^2 character.[13a] If this p–d π interaction is important, the N–S single bond rotation in sulfinimines should be high and the charge distribution should show strong variations during rotation. Reed and Schleyer have shown that in N–S interactions of sulfenamides, and in hypervalent sulfur compounds, the d-orbital participation should not be invoked and the observed high barriers are due to negative hyperconjugation.[14] 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.[3–6] Crystal structures of only two sulfinimines, **3** and **4**, are known. **3** but not **4** has a synperiplanar arrangement. Is there any preference for the C–N–S–O unit of sulfinimine towards synperiplanar arrangement? If so, what is the origin of such a preference? What is the importance of negative hyperconjugation in these molecules? To address these questions and to understand the electron distribution in these molecules, we have performed quantum chemical calculations on **1** and studied the N–S bond rotational path in **1**.

Sulfinimines with unsymmetrical substituents on carbon have been shown to be capable of existing as rapidly equilibrating *E*/*Z* mixtures, because the planar inversion barrier is only 13–17 kcal mol^{-1}.[1,2,14] This is much lower than the N-inversion barrier in methanimine (≈30 kcal mol^{-1}).[15a] The observed small inversion barriers have been attributed to the p–d π interactions in the transition state.[14] The sulfinimines derived from aldehydes are expected to exist only in their *E* conformation.[1,2] Though initially this stability has been attributed to the intramolecular hydrogen bonding,[1] later based on crystal structure data such a possibility was ruled out.[2] Since the d–p π interactions are shown to be unimportant by Reed and Schleyer,[14] what are the reasons for the low N-inversion barriers in sulfinimines? We have been working on the N-inversion barriers, and C=N rotational barriers of several imines and related compounds, to understand the electron distribution in these molecules.[15] In continuation of our efforts, to understand the inversion barriers in sulfinimines and the origin of the preference of the *E* isomer in the aldehyde based sulfinimines, we have performed quantum chemical calculations on **2** and studied the N-inversion process.

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Table 1 Important geometric parameters and total energies (hartrees) of sulfinimine **1**, obtained at various computational levels. Distances in Å, angles in °

Method	NS–S3	S3–O4	N2–S3–O4	C1–N2–S3–H5	C1–N2–S3–O4	Total energy
HF/3-21G	1.826	1.653	104.9	118.3	9.4	−563.368522
HF/6-31G	1.834	1.704	105.7	119.6	12.9	−566.152387
HF/6-31+G	1.831	1.714	105.6	120.0	14.6	−566.163415
B3LYP/6-31+G	2.038	1.686	102.9	112.4	7.8	−567.865456
HF/3-21G*	1.695	1.475	110.3	122.0	11.4	−563.546194
HF/6-31G*	1.700	1.469	111.3	122.4	12.9	−566.329301
HF/6-31+G*	1.699	1.473	111.1	122.3	13.7	−566.338033
MP2/6-31+G*	1.761	1.507	112.1	122.6	14.2	−566.947879
B3LYP/6-31+G*	1.769	1.505	112.3	121.7	13.3	−567.995342
B3PW91/6-31+G*	1.751	1.500	112.4	121.9	13.5	−567.876556

Computational details

Ab initio[16] and Density Functional (DFT)[17] calculations have been carried out using the GAUSSIAN 94W[18] package, the windows version of GAUSSIAN 94 suite of programs, on an IBM compatible PC Pentium-100MHz with 64 MB memory and 1 GB disk space. Complete optimizations have been performed on sulfinimine, **1** methylsulfinimine, **2**, their rotational and *E*/*Z* isomerization conformers and corresponding transition states using the HF/6-31G*[19] basis set. Since these molecules possess four lone pairs and that too on adjacent atoms, inclusion of diffuse functions in the basis set is important[16] and hence all the structures have completely been optimized at HF/6-31+G* level also. To study the effect of electron correlation on the geometries and energies, full optimizations have been performed using MP2/6-31+G* and the density functional method,[17] defining the exchange functionals according to Becke's three parameter formulation (B3)[20a,b] and the correlation functionals according to the Lee, Yang, Parr (LYP) formulation[20c,d] and using the 6-31+G* basis set. Frequencies were computed analytically for all optimized species at HF/6-31G* and HF/6-31+G* levels in order to characterize each stationary point as a minimum or a transition state and to determine the zero point vibrational energies (ZPEs).[21] The ZPE values obtained at HF/6-31G* and HF/6-31+G* levels have been scaled by factors of 0.9135 and 0.9153 respectively.[22] Atomic charges in all the molecules were obtained using the Natural Population Analysis (NPA) method[23] within the Natural Bond Orbital (NBO) model using HF/6-31+G* geometries and MP2/6-31+G** densities to understand the electron distribution in these molecules. Semi-empirical AM1 calculations[24] have been performed on **1**–**4** using the MOPAC package.[25] The geometrical parameters obtained at HF/6-31+G* level and the energies obtained at B3LYP/6-31+G* (+ZPE) level will be used in the discussion unless otherwise specifically mentioned.

Results and discussion

Structures and charges

Theoretical calculations on **1** at various levels have been performed to select a suitable method for sulfinimines and the results are reported in Table 1. Here, the study is mainly focused on the synperiplanar arrangement of **1** because it is the most stable arrangement on the S–N rotational path (see below). The N–S and S=O bond distances are found to be highly sensitive to the method used. The N–S and S–O bond distances are very large when d orbitals are not included in the basis set. After including the d orbitals in the form of polarization functions (HF/6-31+G*), the N–S and S–O distances became comparable to those reported for **3** and **4** using crystallographic methods (Table 2).[2,26] After including the electron correlation, using the MP2, B3LYP and B3PW91 methods, the N–S and S–O distances became longer, due to the overestimation of the repulsive interactions between the lone pairs on N, S and O.[27]

Table 2 Comparison of the important geometrical parameters of **1** and **2** with crystal structure data of **3** and **4**. Distances in Å, angles in °

Parameter	**1**[a]	**2*E***[a]	**2*Z***[a]	**3**[b]	**4**[c]
C1=N2	1.254	1.257	1.258	1.271	1.282
N2–S3	1.699	1.695	1.684	1.704	1.714
S3=O4	1.473	1.475	1.475	1.474	1.484
S3–H5	1.339	1.339	1.336	—	—
O4$\cdots$H6	2.398	2.371	—	2.376	—
C1–N2–S3	117.1	117.5	126.0	116.6	119.6
N2–S3–O4	111.1	111.3	114.8	111.8	103.4
N2–S3–H5(or C5)	91.3	91.6	90.6	—	97.1
C1–N2–S3–O4	13.7	13.7	26.3	≈0[d]	158.0
C1–N2–S3–H5	122.3	122.3	134.4	—	91.9

[a] Theoretical values obtained at the HF/6-31+G* level. [b] From the supplementary material of ref. 2. [c] From ref. 26. [d] Implied from the text of ref. 2.

The important geometrical data of **1**, **2*E*** and **2*Z*** are given in Fig. 1. A comparison of the important geometric parameters of **1**, **2*E***, **2*Z*** (obtained using the HF/6-31+G* method) with the crystal structure data of **3** and **4** is given in Table 2, which shows excellent agreement.

The dihedral angle between the C–N–S and the N–S–O planes in **1** is in the range of 7.8–14.6° at various levels of theory (Table 1). Similarly, the C–N–S–O torsional angles in **2*E*** and **2*Z*** at HF/6-31+G* level are 13.7 and 26.3° respectively (Table 2). The small torsional angles of **1** and **2** are comparable to those of the reported crystal structure of **3**, shown to have *s-cis* arrangement.[2] Stable structures of **1**–**4** have been studied using the semi-empirical AM1 method. These calculations show C–N–S–O torsional angles of 8.9, 7.0, 3.2, 23.0° for **1**–**4** respectively. The N–S bond lengths in **1**, **2*E*** and **2*Z*** respectively are 1.699, 1.695 and 1.684 Å (Fig. 1). These values are only slightly shorter than the N–S single bond distance (1.709 Å) in H_2N–SH, and are much longer than the N=S double bond distance (1.537 Å) in HN=S, both obtained at HF/6-31+G* level. The N–S bond distances in **1**, **2*E*** and **2*Z*** are slightly longer than the N–S single bond length in (1.677 Å) in sulfinamide, H_2N–S(O)H at HF/6-31+G* level.[15e] This indicates that the N–S bond in sulfinimines is of the order of a single bond only.

To understand the electron distribution in these molecules, we have performed atomic charge calculations on **1**, **2*E*** and **2*Z*** using the NPA method; the atomic charges are given in Table 3. From the data it is clear that the sulfur atom has a strong positive charge (more than 1 unit) in all the molecules. This is because two electronegative elements are attached to the highly polarizable sulfur. The oxygen atom is highly electron dense, the charge on it being close to unity in all the structures. This clearly indicates that the S–O bond in sulfinimines is strongly polarized. The S–O interaction may be described as a single bond with an additional electrostatic interaction between

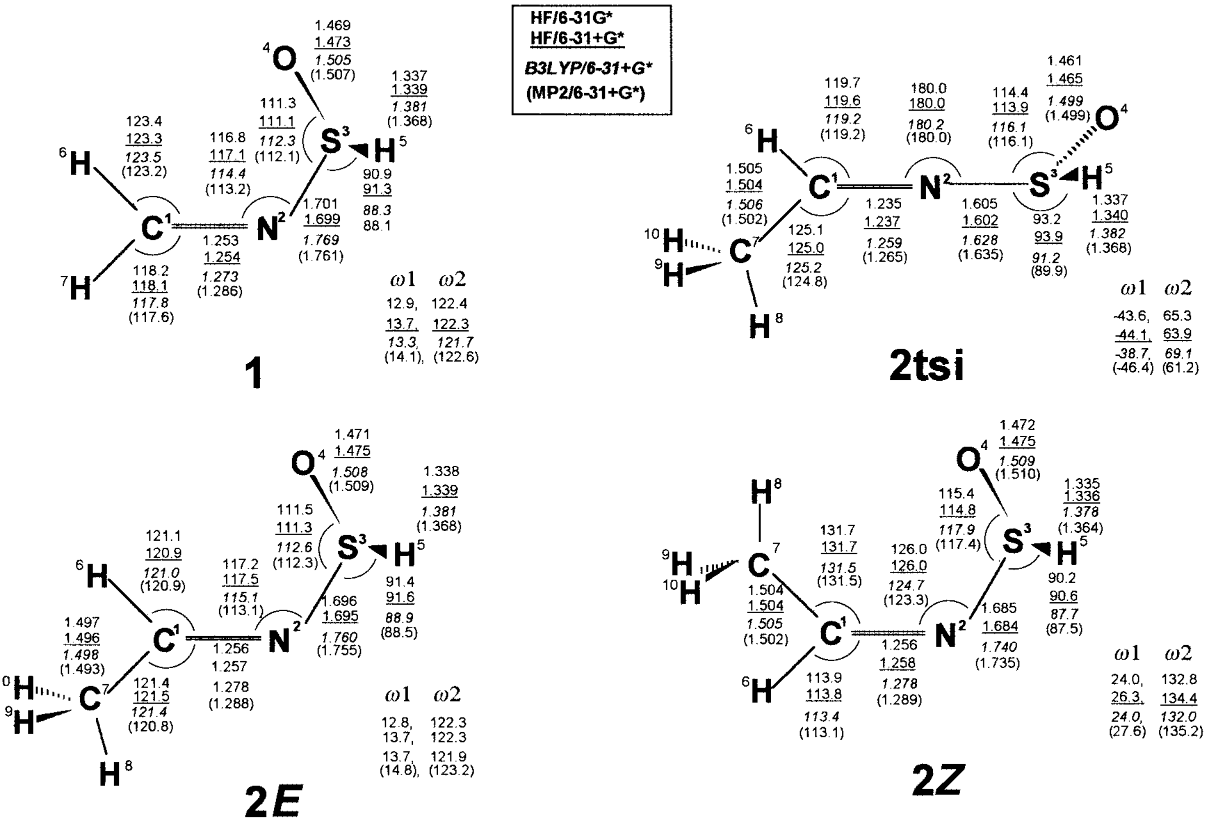


Fig. 1 Important geometric parameters and numbering scheme of sulfinimine **1**, and methylsulfinimine **2*E***, **2*Z***, and the transition state for the N-inversion (**2tsi**) between **2*E*** and **2*Z*** at various levels of *ab initio* calculations. Distances are in Å and angles in °. The C–N–S–O and C–N–S–H torsional angles are represented as ω1 and ω2 respectively.

Table 3 Computed NPA charges on various atoms in **1**, **2*E***, **2*Z*** and **2tsi** obtained at the HF/6-31+G* level using MP2 densities

Atom/group	1	2*E*	2*Z*	2tsi
C1	−0.114	0.103	0.124	0.196
N2	−0.615	−0.666	−0.678	−0.781
S3	1.774	1.241	1.241	1.319
O4	−0.940	−0.974	−0.981	−0.978
H5	0.065	0.054	0.061	0.049
H6	0.210	0.211	0.212	0.182
H7/Me	0.217	0.032	0.021	0.013

the two atoms. This is consistent with similar observations in sulfoxides, sulfonium ylides and sulfilimines.[28] The charges on the hydrogen atoms attached to sulfur in **1** and **2** are only slightly positive whereas those on hydrogen atoms attached to carbon are strongly positive. This indicates that the sulfur atom does not pull electron density from the hydrogen in spite of the strong positive charge on itself. This might originate from the large size of the sulfur atom.

N–S Rotational barriers

To understand the origin for the preference of *synperiplanar* arrangement in sulfinimines,[3–6] we have studied the N–S bond rotational process in **1**.[15e] Complete optimizations at HF/6-31G*, HF/6-31+G* and B3LYP/6-31+G* levels showed that there are three minima corresponding to three rotamers of sulfinimine, **1**, along the N–S bond rotational path. Using the AM1, HF/6-31+G and B3LYP/6-31+G levels, however, we could not locate any N–S bond rotamer for **1**. The geometric parameters of the rotamers, **1r1** (same as **1**), **1r2**, **1r3**, and the three transition states on the N–S bond rotational path **1tsr1**, **1tsr2**, **1tsr3** obtained at HF/6-31+G* are given in Table 4. The absolute energies and ZPE values obtained at various levels are given in Table 5 and the relative energies in Table 6. Fig. 2 shows the potential energy surface for the N–S bond rotational path at various levels. There is a potential well around the rotational structure **1r1**, on the potential energy surface as can be seen from Fig. 2 and Table 6. The N–S bond rotamers **1r2** and **1r3** are 8.90 and 7.20 kcal mol^{-1} higher in energy compared to **1**. The rotamer **1r3** has only a transient existence as indicated by the very small barrier of 0.01 kcal mol^{-1} at HF/6-31+G* level to go to the rotamer **1r1**.[29] The application of ZPE correction results in negative barrier for the conversion of **1r2** to **1r1**. This only reconfirms the transient existence of **1r1**. Though rotamer **1r2** is relatively more stable, the barrier heights for the conversion into **1r1** (0.30 kcal mol^{-1}) and **1r3** (0.88 kcal mol^{-1}) are very small. These small values indicate that **1r2** and **1r3** are thermodynamically unstable.

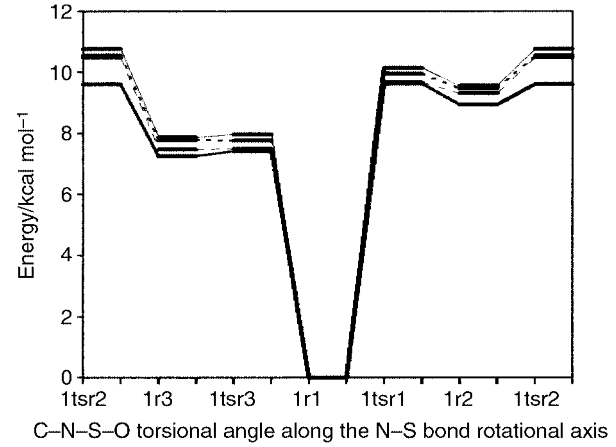


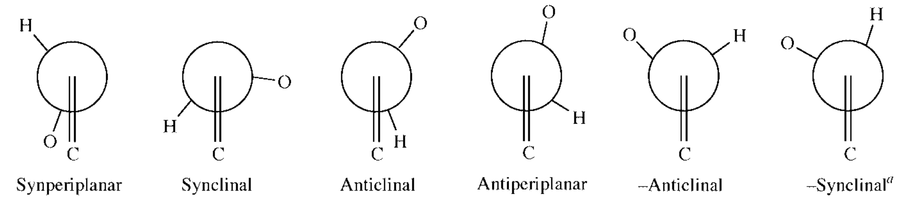
Fig. 2 Potential energy surface for the N–S bond rotational process in sulfinimine, **1**, obtained at HF/6-31G* (—), HF/6-31+G* (.........), B3LYP/6-31+G* (▬▬), MP2/6-31+G*//HF/6-31+G* (- - - -) levels.

1tsr2 with antiperiplanar arrangement has highest energy on the PE surface. **1tsr1** with lone pairs on nitrogen and sulfur *cis*

Table 4 Important geometric parameters of (*R*)-sulfinimine, **1**, its rotamers **1r2**, **1r3** and rotational saddle points **1tsr1**, **1tsr2**, **1tsr3** obtained at the HF/6-31+G* level. Distances are in Å and angles in °. The numbering scheme used is as shown in Fig. 1

Parameter	**1r1**	**1tsr1**	**1r2**	**1tsr2**	**1r3**	**1tsr3**
C1=N2	1.251	1.253	1.251	1.251	1.254	1.255
N2–S3	1.698	1.712	1.699	1.713	1.719	1.720
S3=O4	1.473	1.471	1.467	1.463	1.467	1.469
S3–H5	1.339	1.350	1.351	1.344	1.338	1.337
C1–H6	1.089	1.084	1.085	1.087	1.084	1.084
C1–H7	1.077	1.078	1.078	1.077	1.078	1.078
C1–N2–S3	117.1	118.2	120.3	118.5	114.4	114.3
N2–S3–O4	111.1	108.4	108.3	108.2	108.6	108.8
N2–S3–H5	91.3	95.4	96.0	94.3	91.5	91.5
H6–C1–N2	123.3	124.2	124.3	124.7	124.1	124.2
H7–C1–N2	118.1	118.7	118.8	118.7	118.7	118.7
C1–N2–S3–O4	−13.7	75.9	111.6	164.4	245.2	256.1
C1–N2–S3–H5	−122.3	327.6	2.5	55.7	137.1	148.0
H6–C1–N2–S3	−2.5	1.7	−2.7	−3.4	−0.9	−1.2
H7–C1–N2–S3	178.0	181.9	177.7	176.8	179.0	178.6

Newman Projections



[a] The C–N–S–O torsional angle shows that this is actually in the range of anticlinal.

Table 5 Total energies (hartrees) and zero point energies (kcal mol^{-1}) of sulfinimine **1**, its rotamers and rotational transition states obtained at various computational levels

Compound	HF/6-31+G	B3LYP/6-31+G	HF/6-31G*	HF/6-31+G*	MP2/6-31+G*	B3LYP/6-31+G*	ZPE[a]
1r1	−566.163415	−567.865456	−566.329301	−566.338033	−566.947879	−567.995342	28.28
1r2			−566.314057	−566.323203	−566.932785	−567.981107	27.87
1r3			−566.316765	−566.326103		−567.983794	27.99
1tsr1	−566.143586	−567.845731	−566.313138	−566.322610	−566.932096	−567.979994	27.81
1tsr2			−566.312138	−566.321303	−566.931122	−567.980017	27.57
1tsr3			−566.316607	−566.326082		−567.983516	27.91

[a] Obtained at the HF/6-31+G* level and scaled by 0.9153.[22]

Table 6 Relative energies (in kcal mol^{-1}) of sulfinimine **1**, its rotamers and rotational transition states obtained at various computational levels. The ZPE corrected values are given in parentheses

Compound	HF/6-31+G[a]	B3LYP/6-31+G[a]	HF/6-31G*[b]	HF/6-31+G*[b]	MP2/6-31+G*[a]	B3LYP/6-31+G*[a]
1r1	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
1r2			9.57 (9.11)	9.31 (8.90)	9.47 (9.06)	8.93 (8.52)
1r3			7.87 (7.58)	7.49 (7.20)		7.25 (6.96)
1tsr1			10.14 (9.46)	9.68 (9.20)	9.90 (9.43)	9.63 (9.16)
1tsr2	12.44 (11.73)	12.37 (11.66)	10.77 (9.99)	10.50 (9.78)	10.51 (9.80)	9.62 (8.91)
1tsr3			7.97 (6.91)	7.50 (7.12)		7.42 (7.05)

[a] Corrected using ZPE obtained at HF/6-31+G*. [b] Corrected using ZPE obtained at the same level as that of optimization.

to each other also is equally high in energy. The N–S rotational barriers at HF/6-31G*, HF/6-31+G*, MP2/6-31+G*//HF/6-31+G* and MP2/6-31+G* levels respectively are 10.77, 10.50, 10.55 and 10.51 kcal mol^{-1}. At the B3LYP/6-31+G* level the barrier has been reduced to 9.62 kcal mol^{-1}. After including the ZPE corrections, the values are slightly reduced. At the B3LYP/6-31+G*(+ZPE) level, **1tsr1** becomes the highest energy transition state. When the d-orbital participation is not included (*i.e.* at HF/6-31+G, B3LYP/6-31+G levels) the N–S bond rotational barriers are about 12.4 kcal mol^{-1}. If p–d π interactions are present along the N–S bond, the N–S bond rotational barriers should increase after inclusion of the d orbitals in the basis set. Inclusion of the d orbitals in the form of polarization functions decreases the rotational barrier. This indicates that N–S p–d π interactions are absent in sulfinimines.

The calculated N–S rotational barriers are high compared to single bond rotations of many other bonds. An analysis of the geometrical features of the most stable rotamers of **5**–**7** (Fig. 3) indicates that the lone pairs on nitrogen and sulfur try to be farthest apart, as in **5**.[15e] But when oxygen atoms are involved, structures with the lone pair on N and the oxygen atom *trans* are found to be most stable. Houk *et al.* have reported the conformational PE surface of *N*-methylmethanesulfonamide.[30a]

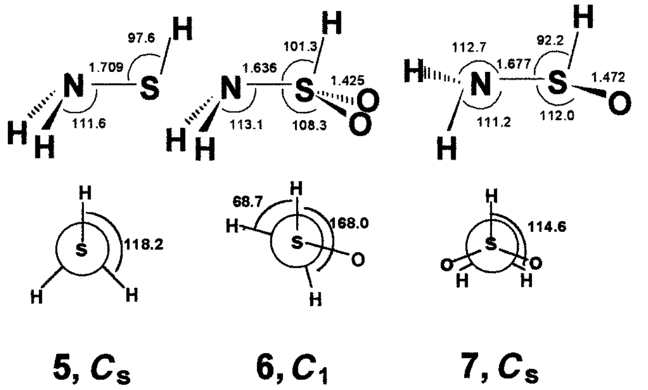


Fig. 3 Important geometrical parameters of the most stable arrangements of sulfenamide, **5**, sulfinamide, **6**, and sulfonamide, **7**, obtained at HF/6-31+G* level. Distances are in Å and angles are in °.

Table 7 Total energies (hartrees) and ZPE values (in kcal mol^{-1}) of **2*E***, **2*Z*** and **2tsi**

Method	**2*E***	**2*Z***	**2tsi**
HF/6-31+G	−605.195836	−605.188599	−605.144107
HF/6-31G*	−605.375659	−605.367155	−605.331358
HF/6-31+G*	−605.384832	−605.375927	−605.341654
MP2/6-31G*//HF/6-31+G*	−606.121885	−606.113324	−606.078140
MP2/6-31+G**//HF/6-31+G*	−606.163799	−606.155281	−606.120032
MP2/6-31+G*	−606.126576	−606.117851	−606.082429
B3LYP/6-31+G*	−607.322206	−607.314783	−607.283602
ZPE[a] (NIF)	45.41 (0)	45.43 (0)	44.50 (1)

[a] A scaling factor of 0.9153 has been used[22] on the values calculated using the HF/6-31+G* level. NIF = Number of imaginary frequencies.

Table 8 Relative energies and N-inversion barriers (in kcal mol^{-1}) of **2** at various computational levels. The ZPE corrected values are given in parentheses

Method	**2*E*** ⟶ **2*Z***	**2*E*** ⟶ **2tsi**	**2*Z*** ⟶ **2tsi**
HF/6-31+G[a]	4.54 (4.50)	32.46 (31.66)	27.92 (27.16)
HF/6-31G*[b]	5.34 (5.37)	27.80 (26.98)	22.46 (21.61)
HF/6-31+G*[b]	5.59 (5.61)	27.09 (26.27)	21.50 (20.66)
MP2/6-31+G*//HF/6-31+G*[a]	5.37 (5.39)	27.45 (26.63)	22.08 (21.24)
MP2/6-31+G**//HF/6-31+G*[a]	5.34 (5.36)	27.46 (26.64)	22.11 (21.27)
MP2/6-31+G*[a]	5.47 (5.49)	27.70 (26.79)	22.23 (21.30)
B3LYP/6-31+G*[a]	4.66 (4.68)	24.22 (23.40)	19.56 (18.72)

[a] ZPE values obtained at the HF/6-31+G* level. [b] ZPE values obtained at the same level as that of optimization.

They also have observed that when the nitrogen lone pair is further away from the oxygen lone pairs unfavorable electrostatic interactions are reduced and such a structure is preferred even though it has an eclipsed arrangement.[30a] Considering this, it may be concluded that in sulfinimines a structure with lowest repulsive interactions between the lone pair on nitrogen and the negatively charged oxygen should be preferred and that is the reason why **1** and **2** have synperiplanar arrangements. In addition, in **1rl**, $n_N \longrightarrow \sigma^*_{SO}$ negative hyperconjugation[14] is present, which gives partial double bond character to the structure. The presence of negative hyperconjugation is evident from the smaller N–S distances, larger N–S–O bond angles and larger N–S bond polarization in **1rl** as compared to the rotamers **1r2** and **1r3**. The energy of stabilization due to the anomeric effect in **1** has been estimated using isodesmic eqn. (1). The stabilization energies at HF/6-31+G*, MP2/6-31+G* and B3LYP/6-31+G* levels respectively are 2.60, 6.20 and 4.94 kcal mol^{-1}.

$$H_2C{=}N{-}S(O)R + NH_3 \longrightarrow H_2N{-}S(O)R + H_2C{=}NH \quad (1)$$

In **1rl** the C–N–S–O torsional angle is −13.7°. When this torsional angle was forced to be 0.0° an increase in energy up to 0.7 kcal mol^{-1} was observed. The deviation from complete planarity might be due to the repulsions between the C=N unit and the S–O unit of the sulfinimines. If repulsions between the C=N and S–O unit are the only reason for this deviation, a structure with a C–N–S–O torsional angle of about +13.7° also should have been observed on the PE surface. However, such an arrangement would increase the proximity of the lone pairs on nitrogen and sulfur and becomes unstable. Hence, a trade off among various repulsive interactions between the lone pairs of electrons on N, S and O and the anomeric effect provides a semi-rigid C–N–S–O backbone for sulfinimines, giving a synperiplanar arrangement, which is responsible for the facial selectivity and stereoselectivity observed in the reactions. The S–N rotational barrier in sulfinimine **1** is higher than that in sulfinamide **6** by about 1.3 kcal mol^{-1} at the HF/6-31+G* level.[15e] This higher barrier might originate from the in plane π character induced by the $n_N \longrightarrow \sigma^*_{SO}$ negative hyperconjugation in **1** which is absent in **6**. In conclusion, there is an out-of-plane C=N π bond, in-plane N–S π character due to negative hyperconjugation in **1** and because these two interactions are in orthogonal planes no C–N–S π delocalization should be expected.

Inversion barriers

In simple sulfinimines the N-inversion and C–N rotation processes go through same transition state and hence the two processes are indistinguishable. The transition state for inversion in **1**, *i.e.* **1tsi**, could be located only at the HF/6-31G* level.[31] To obtain a clear understanding of the inversion process in sulfinimines we have performed calculations on methylsulfinimine, **2**, where the geometrical isomers **2*E*** and **2*Z*** can be clearly distinguished.[31] The absolute energies of **2*E***, **2*Z***, and **2tsi** are given in Table 7 and the relative energies are given in Table 8. The ***Z*** isomer is 4.68 kcal mol^{-1} higher in energy than the ***E*** isomer. The energy difference between **2*E*** and **2*Z*** can mainly be attributed to the repulsions between the Me and S(O)H groups in **2*Z***. The N2–C1–C7 angles in **2*E*** and **2*Z*** at HF/6-31+G* level are 121.5 and 131.7° respectively. Similarly, the C1–N2–S3 angles in **2*E*** and **2*Z*** respectively are 117.5 and 126.0° (Fig. 1). There is a large increase (Table 9) in these two angles as the molecule flips from **2*E*** to **2*Z***. This is due to the increased repulsions between the Me and S(O)H groups in the **2*Z*** arrangement.

The structural features of **2tsi**, the transition state connecting the minima **2*E*** and **2*Z*** are given in Fig. 1.[32] The C1–N2–S3 angle in **2tsi** is close to 180°. In **2tsi** the C=N, N–S, S–O bond lengths have been reduced in comparison to those of **2*E*** (Table 9). This is a consequence of the change of hybridization around N from sp^2 to sp, which increases the s character on the nitrogen and thus the electronegativity of N in **2tsi**. Analysis of the atomic charge data indicates that there is an alternative charge localization in **2tsi** in comparison to that of **2*E*** (Table 9), *i.e.* the positive charges on C and S and the negative charges on N and O have increased appreciably. Hence, the reduction in the C=N, N–S, S–O bond distances can be attributed to the increased coulombic attractions between neighboring atoms.

The inversion barrier in **2*E*** to give **2*Z*** is calculated to be about 27.80 kcal mol^{-1} at the HF/6-31G* level. After including diffuse functions on non-hydrogen atoms, the inversion barrier is slightly reduced to 27.09 kcal mol^{-1}. Inclusion of electron correlation increases the inversion barrier to 27.45 kcal mol^{-1} at the MP2/6-31+G*//HF6-31+G* level. Complete optimizations

Table 9 Variations in important geometric parameters and the atomic charges of **2** during N-inversion. Bond distances are in Å and angles in °. Geometries obtained using the HF/6-31+G* level and charges obtained using MP2/6-31+G** densities

	Geometrical Parameters			Atomic charges			
Parameter	**2*Z*** ⟶ **2tsi**	**2*E*** ⟶ **2tsi**	**2*E*** ⟶ **2*Z***	Atom	**2*E*** ⟶ **2*Z***	**2*E*** ⟶ **2tsi**	**2*Z*** ⟶ **2tsi**
C1=N2	−0.021	−0.021	0.001	C1	0.021	0.093	0.072
N2–S3	−0.082	−0.093	−0.011	N2	−0.013	−0.116	−0.103
S3=O4	−0.010	−0.010	0.000	S3	0.000	0.078	0.078
C1–N2–S3	54.0	62.5	8.5	O4	−0.007	−0.003	0.004
N2–S3–O4	−0.9	2.6	3.5	H5	0.008	−0.004	−0.012
H6–C1–N2	5.8	−1.3	−7.1	H6	0.002	−0.028	−0.030
C7–C1–N2	−6.7	3.5	10.2	C7	−0.034	−0.015	0.019
C1–N2–S3–O4	−70.4	−57.8	12.6	H8	−0.001	0.003	0.004
C1–N2–S3–H5	−70.5	−58.4	12.1	H9	0.020	−0.004	−0.024
H6–C1–N2–S3	68.6	−112.3	179.1	H10	0.004	−0.004	−0.007
C7–C1–N2–S3	68.8	−112.2	−180.9				

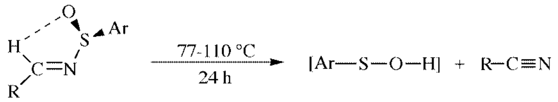
at the MP2/6-31+G* level do not improve the situation. However, the density functional methods at the B3LYP/6-31+G* level reduce the inversion barrier to 24.22 kcal mol^{-1}. After including the ZPE corrections, the inversion barriers are reduced at all levels. The inversion barriers for the reverse process, *i.e.* **2*Z*** ⟶ **2tsi** ⟶ **2*E***, are 21.30 and 18.72 kcal mol^{-1} at MP2/6-31+G* (+ZPE) and B3LYP/6-31+G* (+ZPE) levels respectively. **2*E*** may be considered as a model for the aldehyde derived sulfinimines, where a hydrogen atom is *cis* to the sulfinyl group along the C=N axis and **2*Z*** may be taken as a model for the unsymmetrical sulfinimines[2] where a non-hydrogen group is *cis* to the sulfinyl group. Hence, the energy difference between **2*Z*** and **2tsi** can be compared to the planar inversion barriers reported for the unsymmetrical sulfinimines using the NMR coalescence methods.[2] The theoretically obtained inversion barriers become comparable to the experimentally observed inversion barriers (13–17 kcal mol^{-1}) at the B3LYP/6-31+G* optimization level.

In the absence of d-orbital participation as in the HF/6-31+G level, the inversion barrier is high (32.46 kcal mol^{-1}). This indicates that the d orbitals on sulfur play an important role in reducing the N-inversion barriers in sulfinimines as suggested from the experimental observations.[14] The reduction in the N–S distance during inversion is quite large in **2tsi** in comparison to **2*E*** and **2*Z***. This might be due to the formation of additional π bonds in **2tsi**. To estimate the extent of additional π interactions we have calculated N–S rotational barriers in **2tsi** by performing partial optimization calculations at MP2/6-31+G and MP2/6-31+G* levels. The N–S rotation barrier at the MP2/6-31+G level is 11.08 kcal mol^{-1} and is associated with an increase in the N–S distance by 0.51 Å. After including the d-orbital participation, the N–S rotation barrier increased to about 16.11 kcal mol^{-1} (ΔN–S = 0.056 Å). This indicates that, in **2tsi**, p–d π interactions are present and these stabilize the inversion transition state causing a reduction in the N-inversion barriers in sulfinimines in comparison to simple imines.

The O4 · · · H6 non-bonded distance in **1** is 2.398 Å and in **2*E*** it is 2.371 Å. In **3**, crystal data show that the non-bonded H · · · O distance is 2.376 Å,[2] indicating a good agreement between the experimental and theoretical data. Davis *et al.* have argued that "this non-bonded distance is too large for there to be any hydrogen bonding interaction".[2] O4 is highly negatively charged and H6 is reasonably positively charged. Hence, it is possible that there is some non-bonded electrostatic interaction between the two atoms. Table 10 lists the atomic charges on H6 and O4 in **1** and **1tsr2** and variation in them as a function of the N–S bond rotation. During rotation the negative charge on O4 and the positive charge on H6 decreases, indicating that the electrostatic interaction which is present in **1** gets disrupted on rotation. It should be noted that the H6 in aldehyde derived sulfinimines is not attached to an electronegative element like oxygen but attached to a carbon atom, which is a very weak hydrogen bond donor. The C–H · · · O hydrogen bonding interactions are known in the literature and the hydrogen bond distances in such cases have been reported to be in the range of 2.2–2.9 Å.[33] The observed H6 · · · O4 distances in **1**, **2*E*** and **3** are within the expected range of C–H · · · O hydrogen bond distances and are close to the H · · · O van der Waals distances (2.2 to 2.4 Å) indicating the possibility of electrostatic interactions. The expected stabilization due to such interaction is in the order of 1–2 kcal mol^{-1} only.[29] Formation of sulfenic acids from aldehyde derived sulfinimines on heating (Scheme 1) can be explained only when there is some electrostatic interaction between the H and O atoms.[1b] Hence, the observed preference for the aldehyde derived sulfinimines to show *E* conformation might be attributed to this electrostatic interaction in addition to the minimization of steric repulsions in this configuration.

Table 10 Atomic charges and variations in the atomic charges of **1r1** to **1tsr2** during N–S rotation

	Atomic charges		Variation
Atom	**1r1**	**1tsr2**	**1r1** ⟶ **1tsr2**
O4	−0.973	−0.948	0.025
H6	0.206	0.171	−0.035



Scheme 1

The crystal structure of **3** has a synperiplanar arrangement whereas **4** does not. The difference between the two is only a Me group attached to the iminic carbon atom. From the studies on **2*Z*** it is clear that the bulky Me group causes an increase in the C–N–S–O torsional angle due to the steric interactions between Me and S(O)H. Considering the structure of **4**, we have tried to locate the N–S bond rotamers of **2*Z*** at HF/6-31+G* and AM1 levels: all our efforts proved futile. Dihedral angle constrained optimizations on **2*E*** and **2*Z*** do not show any other minima. Similarly we could not locate any N–S bond rotamers on the PE surface of **4** using the AM1 method. This indicates that, under the gas phase conditions, only the synperiplanar arrangement is preferred for sulfinimines. However, in the solid phase, crystal lattice forces are present in addition to the possibility of intermolecular interactions.[34] These additional forces might result in stability of an isomer of **4** with non-synperiplanar arrangement.

Conclusion

The structural aspects of sulfinimine, **1**, and methylsulfinimine, **2**, the N–S bond rotational isomers of **1**, the *E*/*Z* isomerization pathway of **2** and the charge distribution in them have been studied using *ab initio* and DFT methods. The geometrical parameters for **1** and **2** obtained at the HF/6-31+G* level match well with the crystallographic results for **3** and **4**. There are three minima on the N–S bond rotational path, but two of them can only have a transient existence. The N–S bond rotational barrier in **1** is 9.16 kcal mol^{-1} at the B3LYP/6-31+G* (+ZPE) level. Sulfinimines have a natural tendency to prefer a semi rigid synperiplanar arrangement. The origin of this preference can be attributed to (1) the repulsions among the lone pairs of electrons present on the N, S and O atoms, (2) the $n_N \longrightarrow \sigma^*_{SO}$ negative hyperconjugation and (3) the intramolecular $C–H \cdots O$ electrostatic interactions (only in the case of sulfinimines derived from aldehyde). The semi rigidity of the C–N–S–O unit is responsible for the stereoselectivity and facial selectivity of sulfinimines.

The N-inversion barrier in **2*Z*** is calculated to be 18.72 kcal mol^{-1} at the B3LYP/6-31+G* (+ZPE) level which is comparable to the experimental values. The inversion barriers in sulfinimines are smaller as compared to simple imines. This is due to (1) the lowering of the transition state because of increased d orbital participation in addition to the increased coulombic interactions and (2) the destabilization of the ground state because of increased steric repulsions as a function of the size of the R group *cis* to the sulfinyl group. Atomic charge calculations show that the S–O bond is strongly polar. The sulfinyl group in sulfinimines polarizes the C–N bond while withdrawing electrons through the inductive effect; this leads to the Michael acceptor character of sulfinimines.

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