Electronic structure of *N*-sulfenylimines

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ABSTRACT: The electronic structure of *N*-sulfenylimines was studied in detail using *ab initio* MO and density functional methods. The S—N rotational barriers and N-inversion barriers in HS—N=CH$_2$ at the G2MP2 level were found to be 5.60 and 21.76 kcal mol^{-1}, respectively. There is a partial pπ–pπ bond and a relatively weak n$_N \rightarrow \sigma^*_{S—R}$ anomeric π bond between sulfur and nitrogen in *N*-sulfenylimines. NBO analysis was carried out to estimate quantitatively the above delocalizations in RS—N=CH$_2$ (R = H, Me, Cl, F, BH$_2$) systems. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: *N*-sulfenylimines; pπ–pπ interactions; anomeric interactions

INTRODUCTION

N-Sulfenylimines (**I**) (*N*-alkylidenesulfenamides, sufenimines) are important species belonging to the general class of N–sulfur binding imines, H$_2$C=NSR. Sulfenylimines have been used as intermediates in the synthesis of cephalosporins, cephamycines and carbohydrate derivatives[1] and hence undergo reduction at the iminyl bond and oxidation at sulfur. They undergo nucleophilic addition at the iminyl carbon and electrophilic addition at nitrogen.[2] *N*-Sulfenylimines are used to prepare *β*-lactams, primary amines, etc., by nucleophilic attack at the iminyl carbon.[3] Oxidation of *N*-sulfenylimines give sulfinimines, which are precursors for the asymmetric synthesis of amino acids and many biologically important organic molecules.[4]

The interactions between sulfur and nitrogen in these systems is a topic of special interest. On the one hand we may expect a partial pπ–pπ bond between sulfur and nitrogen because isoelectronic *S*-nitrosothiols (**II**) show *cis–trans* isomerization across this bond.[5] On the other hand, an anomeric π bond due to n$_N \rightarrow \sigma^*_{S—R}$ negative hyperconjugation should be expected as in sulfenamides[6] (**III**). These two interactions are in orthogonal planes and could play an important role.

Davis and co-workers[7] estimated the planar N-inversion barrier in *N*-sulfenylimines and reported that they are smaller than that in imines. The low N-inversion barriers have been attributed to d-orbital participation on sulfur. Our studies on S–N interactions in sulfenamides,[6] sulfonamides[8] and sulfinimines[9] 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. In this paper, we report the electronic structure of *N*-sulfenylimines and address the above aspect.

(I)   (II)   (III)
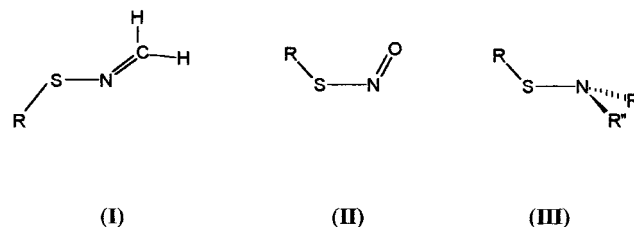
METHODS OF CALCULATIONS

Ab initio MO[10] and density functional theory (DFT)[11] calculations were carried out using the Gaussian 94W[12] package, with the Windows version of the Gaussian 94 suite of programs. Complete optimizations were performed on the conformations of *N*-sulfenylimine **1-c**, **1-t**, rotational transition state **1-rts** and inversion transition state **1-its** using the HF/6–31 + G* basis set. Since these molecules possess several lone pairs of electrons, inclusion of diffuse functions in the basis set is important.[10] To study the effect of electron correlation on the geometries and energies, full optimizations were performed using the MP2(full)/6–31 + G*[13] and B3LYP/6–31 + G*[14] levels also. Frequencies were computed analytically for all optimized species at the HF/6–31 + G*, MP2(full)/6–31 + G* and B3LYP/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 (ZPE). The ZPE values obtained at the HF/6–31 + G*, MP2(full)/6–31 + G*

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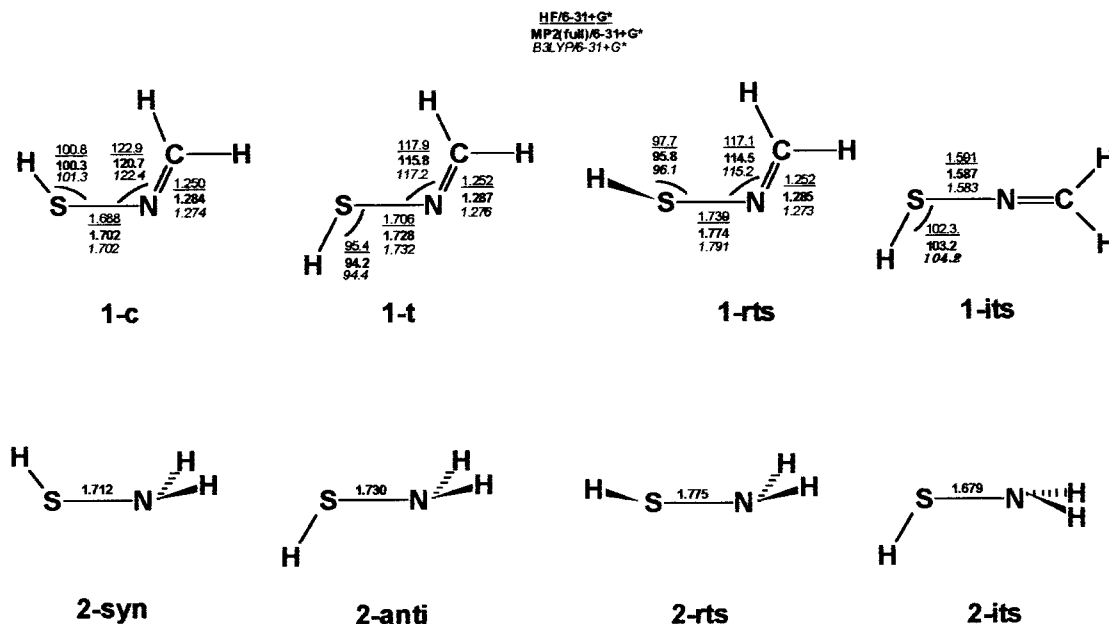
Figure 1. Structures and the geometric parameters of the conformers of sulfenimine **1** and sulfenamide **2** [MP2(full)/6–31 + G* level]

and B3LYP/6–31 + G* levels were scaled by factors of 0.9135, 0.9661 and 0.9806, respectively.[15] The final values of S—N rotational barriers were estimated using the G2MP2[16] and CBS-Q[17] methods.

Atomic charges in all the structures were obtained using the natural population analysis (NPA) method within the natural bond orbital (NBO) approach[18] using the B3LYP/ 6–31 + G* wavefunction. Substituent effects on the S–N interaction were studied on RS—N=CH$_2$ (R = Me, Cl, F, BH$_2$). The solvent effect on the different conformers was also studied at the B3LYP/6–31 + G* level.

RESULTS AND DISCUSSION

The complete optimizations of different conformations of

HSN=CH$_2$ indicated the presence of two minima (*cis*, **1-c** and *trans*, **1-t**, with respect to the S—N bond) and one rotational transition state, **1-rts** and N-inversion transition state, **1-its** (Fig. 1), on the potential energy surface. The structural data corresponding to these structures obtained at the HF/6–31 + G*, MP2(full)/6–31 + G* and B3LYP/6–31 + G* levels are given in Table 1. Both the ground-state structures **1-c** and **1-t** are found to have C_s symmetry. The S—N bond length in **1-c** is 1.688 Å at the HF/6–31 + G* level, increasing to 1.702 Å after including the electron correlation at the MP2 and B3LYP levels. This is consistent with the earlier observation that at electron correlated levels the S—N bond lengths are overestimated.[19] The C=N bond length in **1-c** is 1.284 Å, which is comparable to that in H$_2$C=NH (1.283 Å) at the MP2(full)/6–31 + G* level. The S—N bond length in **1-c**

Table 1. Geometric parameters (distances in Å, angles in degrees) of *N*-sulfinylimine, **1**, at various levels

Parameter	HF/6–31 + G*				MP2(full)/6–31 + G*				B3LYP/6–31 + G*			
	1-c	**1-t**	**1-rts**	**1-its**	**1-c**	**1-t**	**1-rts**	**1-its**	**1-c**	**1-t**	**1-rts**	**1-its**
C=N	1.250	1.252	1.252	1.233	1.284	1.287	1.285	1.261	1.274	1.276	1.273	1.257
S—N	1.688	1.706	1.739	1.591	1.702	1.728	1.774	1.587	1.702	1.732	1.791	1.583
S—H	1.335	1.322	1.328	1.341	1.356	1.338	1.343	1.366	1.367	1.347	1.352	1.386
C—H	1.084	1.083	1.083	1.087	1.097	1.095	1.094	1.098	1.098	1.096	1.096	1.100
C—H	1.077	1.077	1.079	1.087	1.086	1.087	1.089	1.098	1.089	1.089	1.093	1.100
C=N—S	122.9	117.9	117.1	180.0	120.7	115.8	114.5	180.0	122.4	117.2	115.2	180.0
N—S—H	100.8	95.4	97.7	102.3	100.3	94.2	95.8	103.2	101.3	94.4	96.1	104.0
H—C=N	124.3	124.5	124.4	122.0	124.4	125.0	124.7	121.8	124.5	125.4	125.1	121.8
H—C=N	118.3	118.0	117.9	122.0	117.4	116.8	116.8	121.8	117.7	117.0	116.9	121.8
H—S—N=C	0.0	179.9	71.3	—	0.0	180.0	75.0	—	0.0	180.0	75.6	—
H—C=N—S	0.0	0.0	−0.6	—	0.0	0.0	0.0	—	0.0	0.0	−0.3	—
H—C=N—S	180.0	180.0	179.4	—	180.0	180.0	179.9	—	180.0	180.0	179.7	—

Table 2. Absolute energies (a.u.) of the various conformers of *N*-sulfenylimines HSN=CH$_2$, **1**, at various levels

Method	1-c	1-t	1-rts	1-its
HF/6–31 + G*	−491.5242592	−491.5266036	−491.5177586	−491.4881986
MP2(full)/6–31 + G*	−491.9586930	−491.9610768	−491.9509411	−491.9208155
B3LYP/6–31 + G*	−492.8096118	−492.8115026	−492.8006762	−492.7779010
G2MP2	−492.1886555	−492.1895550	−492.1806283	−492.1548708
CBS-Q	−492.2023959	−492.2031821	−492.1940756	−492.1699728
(NIF)[a]	0	0	1	1

[a] NIF = number of imaginary frequencies.

Table 3. Relative energies (kcal mol^{-1}) of HSN=CH$_2$ at various levels, with ZPE corrected values in parentheses

Method	ΔE 1-t → 1-c	Rotational barrier 1-t → 1-rts	Inversion barrier 1-t → 1-its
HF/6–31 + G*[a]	1.47 (1.46)	5.55 (5.15)	24.10 (23.46)
MP2(full)/6–31 + G*[b]	1.49 (1.41)	6.36 (5.91)	25.26 (24.62)
B3LYP/6–31 + G*[c]	1.19 (1.06)	6.79 (6.24)	21.08 (20.44)
G2MP2	(0.56)	(5.60)	(21.76)
CBS-Q	(0.49)	(5.71)	(20.84)

[a] At the HF/6–31 + G* level scaled by 0.9135.
[b] At the MP2(full)/6–31 + G* level scaled by 0.9661.
[c] At the B3LYP/6–31 + G* level scaled by 0.9806.

is shorter than that (1.712 Å) in sulfenamide **2-syn**, suggesting that there is a partial π bond between sulfur and nitrogen in **1-c**. The S—N bond length in **1-t** is longer than that in **1-c** at all levels, e.g. at the MP2(full)/6–31 + G* level the S—N bond length is longer in **1-t** by 0.026 Å. The N—S—H angles in **1-c** and **1-t** are 100.3° and 94.2°, respectively, at the MP2(full)/6–31 + G* level, close to that of divalent sulfur. The shorter S—N bond length and larger N—S—H bond angle in **1-c** relative to **1-t** suggest that there is a strong negative hyperconjugative interaction in **1-c**, because a similar trend was observed between **2-syn** and **2-anti** due to negative hyperconjugation.[6] In the S—N bond rotational transition state (**1-rts**) the S—N bond length is 1.774 Å at

the MP2(full)/6–31 + G* level, an elongation by 0.072 Å with respect to **1-c**. In the N-inversion transition state (**1-its**), the S—N bond length is 1.587 Å, a contraction of 0.115 Å with respect to **1-c** at the same level.

The absolute energies and the relative energies of **1-c, 1-t, 1-rts** and **1-its** at various levels are given in Tables 2 and 3. The energy difference (ΔE) between the *cis* and *trans* isomers in **1** is 1.46 kcal mol^{-1} at the HF/6–31 + G* level. ΔE between **1-c** and **1-t** decreases with increase in the complexity of the quantum mechanical levels. At the G2MP2 and CBS-Q levels the value is 0.56 and 0.49 kcal mol^{-1}, respectively. The S—N rotational barrier in **1** is 5.15 kcal mol^{-1} at the HF/6–31 + G* (+ZPE) level. Inclusion of electron correlation using the

Table 4. Second-order delocalization energy of HSN=CH$_2$ at the MP2(full)/6–31 + G* level

Structure	Delocalization	$n_N \rightarrow \sigma^*_{S-H}$	$n_S \rightarrow \sigma^*_{C-N}$	$n_S \rightarrow \pi^*_{C-N}$
1-c	$E^{(2)a}$	5.56	4.18	21.87
	ΔE^b	1.01	1.70	0.55
	F_{ij}^c	0.07	0.07	0.10
1-t	$E^{(2)a}$	1.69	0.06	18.57
	ΔE^b	1.07	1.70	0.55
	F_{ij}^c	0.04	0.03	0.09
1-rts	$E^{(2)a}$	—	0.67	—
	ΔE^b	—	1.70	—
	F_{ij}^c	—	0.08	—
1-its	$E^{(2)a}$	17.95	11.15	43.75
	ΔE^b	0.80	1.77	0.55
	F_{ij}^c	0.11	0.13	0.12

[a] Second order energy (kcal mol^{-1}).
[b] Energy difference between the two molecular orbitals (a.u.).
[c] Fock matrix element (a.u.).

Table 5. Natural population analysis (NPA) of HSN=CH$_2$ at the MP2(full)/6–31 + G* level

Atom	1-c	1-t	1-rts	1-its
C	−0.072	−0.067	−0.019	−0.098
N	−0.621	−0.622	−0.625	−0.705
S	0.233	0.164	0.136	0.367
H	0.073	0.133	0.114	0.076
H	0.173	0.181	0.186	0.184
H	0.212	0.210	0.207	0.176

Table 7. Lone pair occupancies and second-order delocalization in **1-r** and **1-its** at the MP2(full)/6–31 + G* level

Parameter	1-t	1-its
Occupancies		
n_N	1.961	1.873
RY*$_{(S)}$	0.004	0.016
$E^{(2)a}$		
$n_N \rightarrow \sigma^*_{S—H}$	1.71	17.95
$n_N \rightarrow \sigma^*_{RY(s)}$	2.54	11.38

[a] Second-order energy in kcal mol^{-1}.

Møller–Plesset method increases the rotational barrier by 0.76 kcal mol^{-1}, but the inclusion of electron correlation using the density functional B3LYP method increases the barrier by 1.09 kcal mol^{-1}. At high-accuracy G2MP2 and CBS-Q levels the rotational barrier is 5.60 and 5.71 kcal mol^{-1}, respectively. The S—N rotational barrier in **1** (5.60 kcal mol^{-1}) is less than that in to sulfenamide **2-anti** (6.57 kcal mol^{-1} at the G2MP2 level). The smaller rotational barrier in **1** than **2** may be due to weaker negative hyperconjugative interactions in **1**. NBO analysis (Table 4) in **1-c** 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^{-1}. In **1-t** this negative hyperconjugative interaction becomes very weak [$E^{(2)} = 1.69$ kcal mol^{-1}] and in **1-rts** it becomes negligible. Because of the weaker negative hyperconjugation, the S—N bond length in **1-t** is longer than that in **1-c**.

The atomic charges obtained using the NPA method are given in Table 5. In **1-c** there is a strong negative charge on nitrogen (−0.621) and a positive charge on sulfur (0.233). During rotation the S—N bond polariza-

Table 6. Geometric parameters, rotational barriers, charges and second-order delocalizations of **1** and **2** at the MP2(full)/6–31 + G* level

Parameter	Sulfenimine (1-t)	Sulfenamide (2-anti)
S—N bond length[a]	1.728	1.730
H—S—N bond angle[b]	94.2	96.5
S—N rotational barrier[c]	5.91	8.09
S—N BDE[d]	56.07	66.14
Atomic charges		
S	0.164	0.116
N	−0.622	−1.073
NBO analysis		
$n_N \rightarrow \sigma^*_{S—R}$		
$E^{(2)e}$	1.69	4.60
ΔE^f	1.07	0.97
$F_{ij}{}^g$	0.04	0.06

[a] In Å
[b] In degrees
[c] In kcal mol^{-1}.
[d] Bond dissociation energy at G2MP2 level in kcal mol^{-1}.
[e] Second-order energy in kcal mol^{-1}.
[f] Energy difference between the molecular orbitals in a.u.
[g] Fock matrix elements in a.u.

tion decreases in **1-t** compared with that in **1-c**, in accordance with the observed changes in the negative hyperconjugation. NBO analysis shows a second-order delocalization due to $n_S \rightarrow \pi^*_{C=N}$ interaction in **1-c** [$E^{(2)} = 21.87$ kcal mol^{-1}]. This delocalization 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*-sulfenylimines. These two are in orthogonal planes, i.e. the pπ–pπ bond is perpendicular to the molecular plane and the anomeric π bond is in the molecular plane. During S—N rotation both of these interactions become destroyed, increasing the S—N bond length, and are responsible for the rotational barrier. However, the S—N rotational barrier in **1** is weaker than that in sulfenamide **2-anti**, which has only anomeric π character. This analysis suggests that the combined strength of the partial pπ–pπ bond and the anomeric π bond in **1-c** is weaker than the anomeric π interaction in **2-anti**. This is surprising because the pπ–pπ bond strength is in general expected to be larger than the anomeric π bond strength. To verify this observation, we estimated the S—N bond dissociation energy (Table 6) in **1-c** and **2-anti**, which are 56.07 and 66.14 kcal mol^{-1}, respectively, at the G2MP2 level. The smaller S—N bond dissociation energy in **1-c** confirms that the S—N bond strength is weaker than that in **2-anti**. The 3p–2p interaction leading to a pπ–pπ bond is weak because of the smaller overlap between the 3p and 2p orbitals. The anomeric π bond is also very weak because the sp^2-hybridized nitrogen in **1-c** does not have freedom for inversion and partial rehybridization. Such a freedom is available in **2-anti**. Hence the combined strength of the partial pπ–pπ bonds in **1-c** is weaker than the anomeric π interactions in **2-anti**.

The planar N-inversion barrier in **1** is 21.76 kcal mol^{-1} (20.84 kcal mol^{-1}) at the G2MP2 (CBS-Q) level. These values are comparable to the experimental estimate of the planar N-inversion barrier (20.3–20.8 kcal mol^{-1}) in arylsulfenimines, XC$_6$H$_4$SN=CMe$_2$ (X = H, 4-Cl, 4-Br, 3-NO$_2$, 4-NO$_2$).[7] These values are lower than that in imines CH$_2$=NR ($\sim$30–32 kcal mol^{-1}). Davis and Kluger[7b] rationalized this observation in terms of the donation of electrons from nitrogen to the d-orbital on sulfur. In the two ground states (**1-c**, **1-t**) and during the S—N bond rotation (i.e. in **1-rts**), the d-orbital

Table 8. Geometric parameters, rotational barriers, N-inversion barriers and second-order delocalizations of substituted sulfenimines RSN=CH$_2$ at the B3LYP/6–31 + G* level

Parameter	R = H (**1-c**)	R = Me (**4-c**)	R = Cl (**5-c**)	R = F (**6-c**)	R = BH$_2$ (**7-c**)
S—N bond length[a]	1.702	1.694	1.621	1.599	1.761
C=N bond length[a]	1.274	1.277	1.275	1.278	1.272
R—S—N bond angle[b]	101.3	107.2	109.3	108.0	108.0
S—N=C bond angle[b]	122.4	124.3	132.4	134.3	118.3
S—N rotational barrier (water)[c]	6.79 (6.24)	7.53 (6.37)	13.78 (13.06)	15.56 (14.17)	3.35 (3.49)
$E^{(2)}$[d] $n_N \rightarrow \sigma^*_{S—R}$	1.02	6.38	22.77	22.93	3.17
$E^{(2)}$[d] $n_s \rightarrow \pi^*_{C=N}$	15.09	21.84	27.78	32.69	—

[a] In Å.
[b] In degrees.
[c] In kcal mol^{-1}.
[d] Second-order energy in kcal mol^{-1}.

participation has been found to be negligible. However, in the inversion transition state **1-its**, the d-orbital occupancy increased significantly. For example, the d-orbital population in **1-t** is 0.004 and in **1-its** it is 0.016. In fact, the $n_N \rightarrow RY^*_{(S)}$ delocalization in **1-its** amounts to 11.38 kcal mol^{-1} and $n_N \rightarrow \sigma^*_{S—H}$ delocalization amounts to 17.95 kcal mol^{-1} (much larger than that in **1-t**) (Table 7). Hence it may be concluded that in **1-its** the d-orbital participation and negative hyperconjugative interactions together play an important role. NBO analysis (Table 4) 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 $n_S \rightarrow \pi^*_{C=N}$ delocalization (17.95 and 43.75 kcal mol^{-1}, respectively). The decrease in the S—N and C=N bond lengths (1.587 and 1.261 Å, respectively) in **1-its** is indicative of an increase in bond order between the respective atoms. The high inversion barrier relative to the rotational barrier seems to be the result of an increase in lone pair–lone pair repulsions between sulfur and nitrogen in **1-its**. The high inversion barrier makes the transformation of **1-c** to **1-t** improbable through inversion and it rather occurs through rotation.

The importance of anomeric interactions in *N*-sulfenylimines can be understood from the studies of the substituents effect. The S—R σ^* energy decreases with increase in the electronegativity on R, hence the ΔE between $\sigma^*_{S—R}$ and n_N also decreases. This is manifested in the form of an increased $n_N \rightarrow \sigma^*_{S—R}$ delocalization energy.

Table 8 shows the important geometric, energetic and electronic parameters for RS—N=CH$_2$ systems (R = H, **1-c**; Me, **4-c**; Cl, **5-c**; F, **6-c**; BH$_2$, **7-c**). The S—N bond length gradually decreases with increase in electronegativity of R. The S—N rotational barrier increases in the same order. The second-order energy $E^{(2)}$ due to $n_N \rightarrow \sigma^*_{S—R}$ negative hyperconjugation increases in the same order. The electropositive substituents decrease the negative hyperconjugative effect as indicated by the BH$_2$ group. All these points indicate an increase in the anomeric π strength with increase in the electronegativity of the substituents. $n_S \rightarrow \pi^*_{C=N}$ delocalization also increases in the order **7** < **1** < **4** < **5** < **6**. This shows

the increase in the pπ–pπ strength also in the substituted *N*-sulfenylimines in the *cis* conformation. The decrease in the S—N rotational barrier in water medium also emphasizes the importance of anomeric interactions in *N*-sulfenylimines.

CONCLUSIONS

Theoretical studies showed that *N*-sulfenylimines possess two types of partial π bonds, (a) due to pπ–pπ interactions between sulfur and nitrogen arising from the $n_S \rightarrow \pi^*_{C=N}$ electron delocalization and (b) due to an anomeric π bond arising from the $n_N \rightarrow \sigma^*_{S—R}$ interactions. The anomeric π strength in *N*-sulfenylimines is much weaker than that in sulfenamides. The S—N rotational barrier in substituted *N*-sulfenylimines increases with increase in electronegativity of the substituents. The pπ–pπ interactions and anomeric π interactions increase in **1-its**, which leads to a lower inversion barrier relative to imine and the N-inversion barrier decreases in the same order, comparable to the experimentally observed values.

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