Bull. Chem. Soc. Jpn., ***78***, *1417–1424 (2005)* 1417

Electronic Structure of Sulfimides: A Theoretical Study

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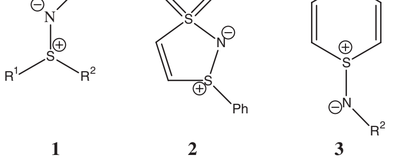
The electronic structure of sulfimides has been studied using the model system $HN{=}SH_2$, **1**, by performing ab initio calculations. There are two minima on the path of rotation across the S–N bond in **1**. G2 calculations showed that the S–N rotational barrier in **1** is 8.50 kcal/mol. The inversion around S in **1** goes through a high-energy barrier of 26.85 kcal/mol at the same level. Substituent effects on the electronic structure were studied using Me, Cl, and F as substituents. Charge analysis using the NPA method has been performed to understand the electronic factors responsible for the observed trends in the S–N interactions. The NBO method was employed to quantitatively estimate the second-order interactions, which indicate that the S–N partial double-bond character in sulfimides is mainly attributable to negative hyperconjugative interactions, rather than $p\pi$–$p\pi$ interactions.

Sulfimides ($RN{=}SR^1R^2$), **1**, also known as sulfimides or iminosulfuranes, have important medicinal applications as antimicrobial, antidepressants, diuretic, hypotensive, and tumour growth inhibitor and as stimulants on the nervous system.[1–9] They have gained importance in organic synthesis due to the presence of two reaction sites, S and N, which can be attacked by nucleophiles and electrophiles, respectively. Though sulfimides have been known since 1917, there is renewed interest in these compounds with the recognition that they are useful as methylidene transfer reagents.[2] Also important is the development of procedures for the enantioselective synthesis of these compounds.[3] The few selected examples given below illustrate the importance of this class of sulfur nitrogen ylids. The synthesis of novel sulfimides and identifying their applications continues to be a fascinating subject.[4] Lithiated sulfimides have been employed as nucleophiles in aromatic substitution reactions.[5] Several heterocyclic compounds can be prepared using sulfimides; compounds with endocyclic[8] **2** and exocyclic **3** sulfimides functional groups have been reported (Chart 1).[1,6] The synthesis of sulfimides from unsymmetrically substituted sulfides leads to two optically active forms. The optical activity of the sulfimides has been assigned to a high inversion barrier at S.[3b] Allylic sulfimides are known to undergo a rearrangement to give sulfimides.[2b] Complexation reactions of sulfimides with a series of transition metals has been reported.[7] Rollin and co-workers recently reported the synthesis of anomeric sulfimides, and showed their application as glycosyl donors.[8] Fujii et al. reported that sulfimides with S=N double bond when treated with Selectfluor can yield fluoro-λ^6-sulfanenitrile with an S≡N triple bond.[9]



1 **2** **3**

X=O. S. NMe. NPh

Chart 1.

There has been some controversy as to whether the sulfimides S=N linkage is a double bond or a semipolar bond.[1a,1e] The crystallographically observed S–N bond lengths vary very strongly between 1.51 to 1.64 Å, sulfimides with halogen substituents on sulfur showing smaller distances. In many cases the S–N bond lengths are with the limits of the S–N double bond length, and there should be some amount of S–N π interaction in these molecules, however, much reduced it may be. The S=N rotational barriers in sulfimides are expected to be small because of the hypervalent nature of the sulfur atom and the ionic character of the S–N interaction. Reed and Schleyer have shown that the 3d orbital participation in sulfur is negligible, even in hypervalent sulfur systems;[10] hence, the $d\pi$–$p\pi$ bond should not be expected in sulfimides. Politzer et al. have studied the electrostatic potential of *S*,*S*-dimethyl-*N*-(2-pyrimidinyl)sulfimides using the STO-5G method.[11] Klein et al. studied the conformational preferences of *N*-tosylsulfimides using the semiempirical method.[12] Shimizu et al. have reported that the pyramidal S-inversion in $R_2S{=}NR$ is smaller than the Se-inversion in $R_2Se{=}NR$ and the Te-inversion in $R_2Te{=}NR$, using density functional studies.[13] The structures and conformations of a series of halo and formyl substituted sulfimides have been reported by Oberhammer and co-workers.[14] Harmata et al. reported on the theoretical analysis of 2,3-sigmatropic shifts in allylic sulfimides.[15] Burtzoff et al. studied the preferred connectivity of molecules containing a sulfur–nitrogen bond using the B3LYP/6-311+G* method. They reported that electronegative substituents, like fluorine, increase the stability of the $FN{=}SF_2$ systems relative to its isomers. For example $FN{=}SF_2$ is more stable than FN–SF.[16] Collins and Duke carried out a comparative study of some structures containing nitrogen–sulfur compounds, such as NSF,

Published on the web August 4, 2005; DOI 10.1246/bcsj.78.1417

HSN, N_2S, N_2S_2, and H_3NS.[17] Mezey et al. studied the conformational analysis of a simple sulfimides model, and also studied a steric and lone-pairs effects on *S*,*S*-dimethyl-*N*-methyl sulfonylsulfimide.[18] None of the previous works reported about the π strength across S and N in sulfimides. Our recent work suggested that negative hyperconjugation is a very important factor across the S–N single bond.[19] Herein, we report on ab initio studies concerning the conformational aspects of sulfimides, $H_2S{=}NH$, **1**. Charge analysis, second-order interactions, and substituent effects in **1** have been explored. Comparisons have been made between S–N interactions in sulfimides and sulfinamides.

Methods of Calculations

Ab initio MO[20] and density functional[21] (DFT) calculations have been carried out using the Gaussian 98W[22] package. Complete optimizations have been performed on sulfimides **1**, its rotational conformer **1-r** and the S–N rotational, S-inversion transition states using the HF/6-31G*, B3LYP/6-31+G*, and MP2(full)/6-31+G* levels (Fig. 1) Frequency calculations have been performed 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* level have been scaled by a factor of 0.9153.[23] In order to obtain accurate values of the S–N bond rotation barriers, single-point calculations have been performed at various levels of ab initio calculations, including QCISD(T)[24] and CCSD(T)[25] methods. The final energies have been obtained using the G2 method[26] Table 1 (also see Tables S1 and S2 in Supplementary Information). The atomic charges in all the structures were obtained using the natural population analysis (NPA) method within the natural bond orbital approach,[27] using the MP2(FULL)/6-31+G* geometries to understand the electron distribution in these molecules. The second-order interactions reported in this work are also based on the above NBO analysis (Table 2). To study the substituent effect on the structure and conformations, ab initio MO, DFT, and NPA calculation were performed on $R_2S{=}NH$ (**2**–**4**) and on $H_2S{=}NR$ (**5**–**7**), where R is F, Cl, and CH_3 (Fig. 2). The results were compared with sulfinamides **8**–**14** to gain an understanding of the S–N interactions (Fig. 3). The geometric parameters and second-order interactions obtained at the MP2(full)/6-31+G* level and the G2 (thermal free) energy values are employed in this discussion unless otherwise specifically mentioned.

Results and Discussion

Concerning the potential energy surface of sulfimides, $HN{=}SH_2$, two minima, **1** and **1-r** one S–N rotational transition state, **1-rts**, and one S-inversion transition state **1-its** could be located. The structural data corresponding to these structures obtained using the HF/6-31+G*, B3LYP/6-31+G*, and MP2(full)/6-31+G* levels are given in Fig. 1. Both the ground-state structure **1** and **1-r** are found to have C_s symmetry. The basic difference between the two structures arises from the arrangement of the SH_2 group, *syn* or *anti* with respect to the N–H bond. The S–N bond length in **1** is 1.576 Å at the HF/6-31+G* level; this distance increases to 1.594 Å and 1.588 Å after including the electron correlation at the B3LYP and MP2 level. The S=N bond length (1.588, at MP2 level) in **1** is much shorter than the S–N single-bond length in HS–NH_2 (1.712 Å), and also slightly shorter than the S–N double bond length in S=NH (1.594 Å), both obtained at the MP2(full)/6-31+G* level. The N–S–H and S–N–H angles in **1** are 113.7° and 112.6°, respectively at the MP2(full)/6-31+G* level, comparable to the experimentally observed values. The S–N bond length in **1-r** is 1.606 Å at the MP2(full)/6-31+G* level, which is slightly longer than that in **1**. The N–S–H angle in **1-r** (108.0°) is much smaller than that in **1**. In rotational transition state **1-rts**, the S–N distance increases only by ~0.018 Å, indicating that during rotation the S–N bond elongation is very small, i.e., there is no significant change in the S–N interaction during S–N rotation in sulfimides. The S–N bond length strongly increases during

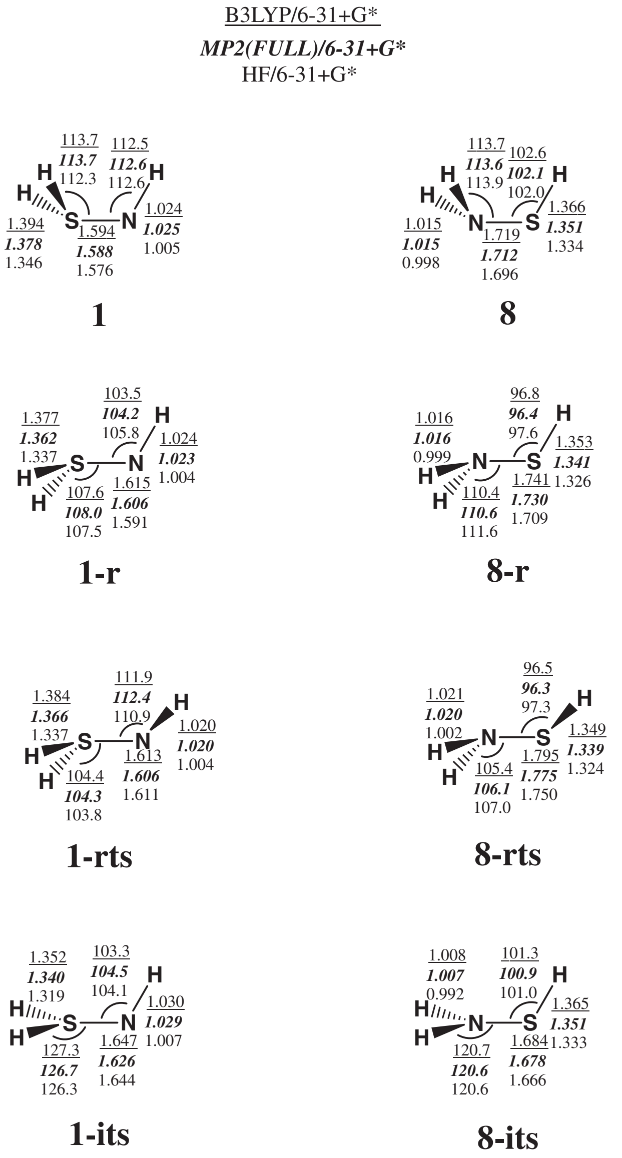


Fig. 1. Important geometrical parameters of sulfimides **1**, and sulfinamide **8** and its rotamer **1-r**, **8-r**, rotational transition state **1-rts**, **8-rts** and inversion transition state **1-its**, **8-its** at HF/6-31+G*, ***MP2(FULL)/6-31+G****, and B3LYP/6-31+G* levels.

Table 1. The Relative Energies between Various Isomers of **1–14** (in kcal/mol, ZPE Values Included after Scaling)

$H_2S{=}NH$	**1**	**1-r**	**1-rts**	**1-its-S**
B3LYP/6-31+G*	0.00	1.61	9.24	26.00
MP2(full)/6-31+G*	0.00	1.22	10.12	27.00
G2 FREE ENERGY	0.00	0.93	8.50	26.85
$H_2S{=}NF$	**2**	**2-r**	**2-rts**	**2-its-S**
B3LYP/6-31+G*	0.00	6.53	15.66	21.90
MP2(full)/6-31+G*	0.00	6.86	16.73	22.75
G2 FREE ENERGY	0.00	5.89	16.13	23.30
$H_2S{=}NCl$	**3**	**3-r**	**3-rts**	**3-its-S**
B3LYP/6-31+G*	0.00	6.57	14.30	24.91
MP2(full)/6-31+G*	0.00	7.02	15.42	26.86
G2 FREE ENERGY	0.00	6.18	13.54	27.28
$H_2S{=}NMe$	**4**	**4-r**	**4-rts**	**4-its-S**
B3LYP/6-31+G*	0.00	6.91	12.26	29.43
MP2(full)/6-31+G*	0.00	6.87	13.45	30.57
G2 FREE ENERGY	0.00	6.40	11.98	30.10
$F_2S{=}NH$	**5**	**5-r**	**5-rts**	**5-its-S**
B3LYP/6-31+G*	0.00	7.14	11.11	20.14
MP2(full)/6-31+G*	0.00	7.28	12.05	22.08
G2 FREE ENERGY	0.00	4.38	10.19	23.40
$Cl_2S{=}NH$	**6**	**6-r**	**6-rts**	**6-its-S**
B3LYP/6-31+G*	0.00	10.01	9.46	66.09
MP2(full)/6-31+G*	0.00	10.48	9.94	69.95
G2 FREE ENERGY	0.00	7.35	8.71	64.18
$Me_2S{=}NH$	**7**	**7-r**	**7-rts**	**7-its-S**
B3LYP/6-31+G*	0.00	−0.58	7.70	32.33
MP2(full)/6-31+G*	0.00	−1.36	8.08	35.55
G2 FREE ENERGY	0.00	−1.36	7.13	34.39
$HS{-}NH_2$	**8**	**8-r**	**8-rts**	**8-its-S**
B3LYP/6-31+G*	0.00	0.84	7.78	1.83
MP2(full)/6-31+G*	0.00	1.21	8.23	2.13
G2 FREE ENERGY	0.00	0.21	6.66	1.90
$HS{-}NF_2$	**9**	**9-r**	**9-rts**	**9-its-S**
B3LYP/6-31+G*	0.00	0.65	3.97	28.25
MP2(full)/6-31+G*	0.00	1.01	4.58	33.56
G2 FREE ENERGY	0.00	0.05	3.88	29.08
$HS{-}NCl_2$	**10**	**10-r**	**10-rts**	**10-its-S**
B3LYP/6-31+G*	0.00	1.44	5.01	8.76
MP2(full)/6-31+G*	0.00	1.46	6.03	10.22
G2 FREE ENERGY	0.00	1.33	4.95	9.71
$HS{-}NMe_2$	**11**	**11-r**	**11-rts**	**11-its-S**
B3LYP/6-31+G*	0.00	1.86	7.26	4.44
MP2(full)/6-31+G*	0.00	1.87	7.39	6.24
G2 FREE ENERGY	0.00	2.12	7.11	5.22
$FS{-}NH_2$	**12**	**12-r**[a)]	**12-rts**	**12-its-S**[a)]
B3LYP/6-31+G*	0.00	—	20.00	—
MP2(full)/6-31+G*	0.00	—	20.45	—
G2 FREE ENERGY	0.00	—	18.33	—
$ClS{-}NH_2$	**13**	**13-r**[a)]	**13-rts**	**13-its-S**[a)]
B3LYP/6-31+G*	0.00	—	17.46	—
MP2(full)/6-31+G*	0.00	—	16.46	—
G2 FREE ENERGY	0.00	—	14.31	—
$CH_3S{-}NH_2$	**14**	**14-r**	**14-rts**	**14-its-S**
B3LYP/6-31+G*	0.00	−0.85	7.00	—
MP2(full)/6-31+G*	0.00	−1.21	7.02	0.80
G2 FREE ENERGY	0.00	−0.53	6.81	1.24

a) There structure could not be identified on the respective PE surfaces (Ref. 19c). Result on **8–14** have been reported earlier in Ref. 19c.

Table 2. Energy $E^{(2)}$ Associated with Important Second-Order Electron Delocalization in **1**–**14**

	1	**2**	**3**	**4**	**5**[a)]	**6**	**7**
$n1_S \rightarrow \sigma^*_{N\text{–}X}$	5.74	8.92	9.43	4.90	8.61	8.73	6.64
$n1_N \rightarrow \sigma^*_{S\text{–}X}$	6.75	2.42	3.60	6.41	12.52	20.14	5.50
$n2_N \rightarrow \sigma^*_{S\text{–}X}$	22.35	18.05	18.17	23.58	—	60.66	21.46
	8	**9**	**10**	**11**	**12**	**13**	**14**
$n1_S \rightarrow \sigma^*_{N\text{–}X}$	1.86	1.31	2.83	1.91	2.45	2.33	2.00
$n2_S \rightarrow \sigma^*_{N\text{–}X}$	3.78	10.02	7.13	2.24	7.48	6.05	4.26
$n1_N \rightarrow \sigma^*_{S\text{–}X}$	8.09	2.34	4.47	8.26	35.91	30.82	8.60

X = 1, 8 = H; 2, 5 = F; 3, 6 = Cl; 4, 14 = Me. a) An S–N double bond was shown by NBO in 5.

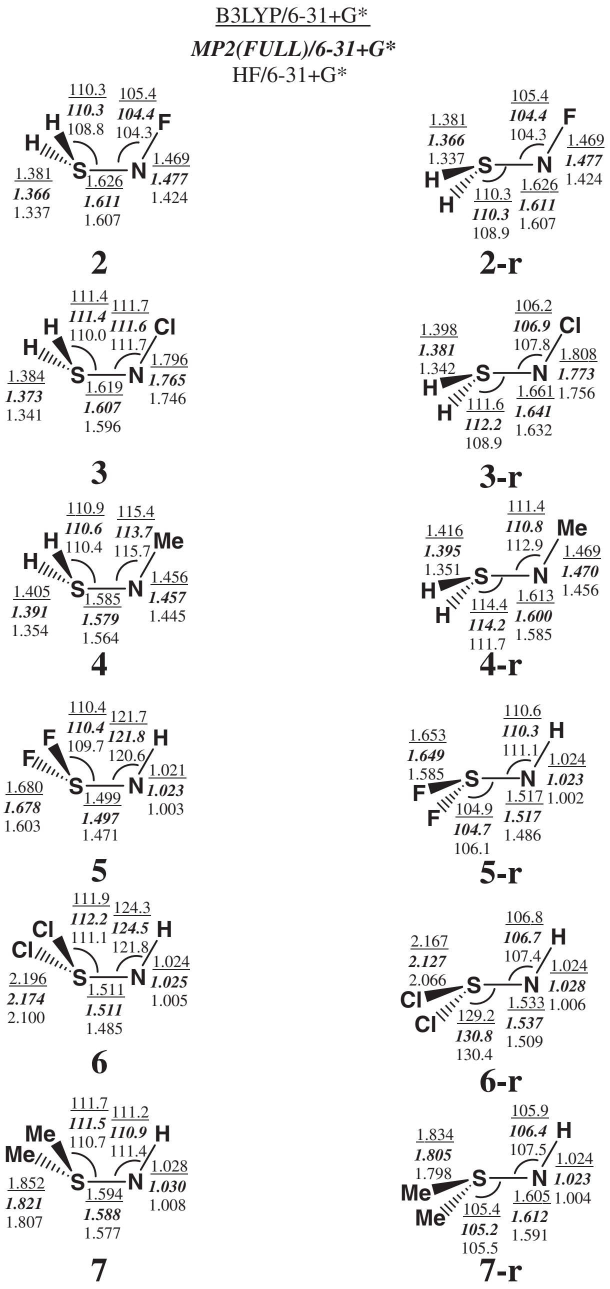


Fig. 2. Important geometrical parameters of sulfimides **2**–**7**, and its rotamer **2-r** to **7-r**, at HF/6-31+G*, ***MP2(FULL)/6-31+G**** and B3LYP/6-31+G* levels.

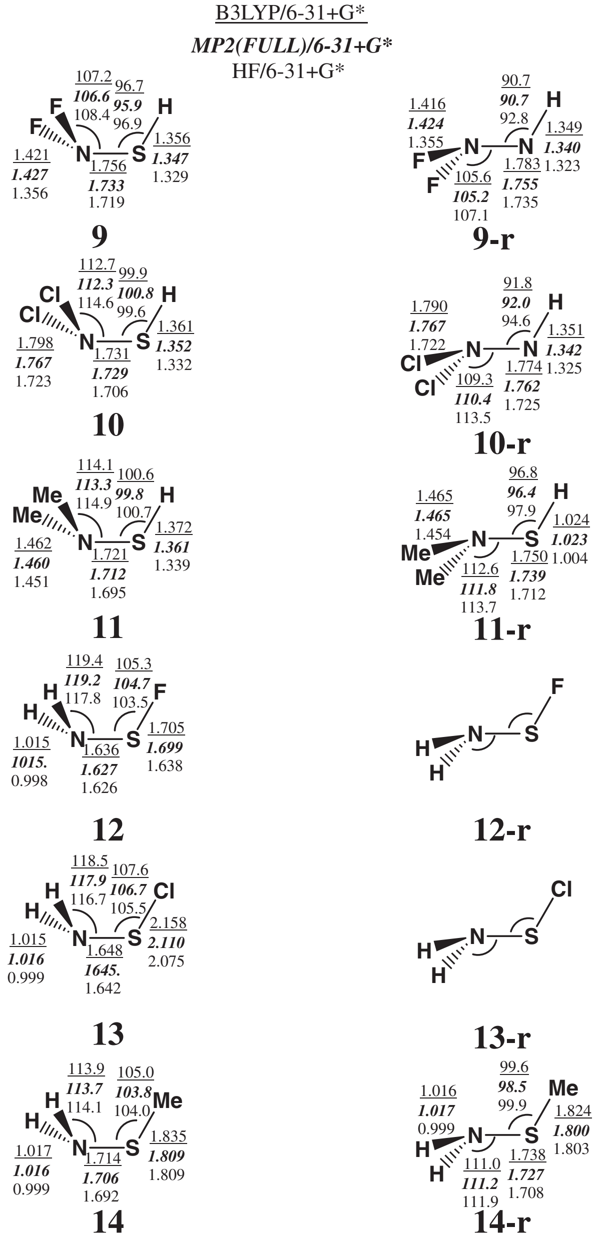


Fig. 3. Important geometrical parameters of sulfinamide **9**–**14**, and its rotamer **9-r** to **14-r**, at HF/6-31+G*, ***MP2(FULL)/6-31+G**** and B3LYP/6-31+G* levels. **12r** and **13r** could not be located on the respective PE surfaces, owing to severe lone-pair lone-pair repulsions.

inversion, as in **1-its** (by 0.038 Å).

The absolute energies of **1** and its related structures are given in Supplementary Information; the relative values are given in Table 1. Conformation **1** with a *syn* arrangement of hydrogen is the most stable. The corresponding *anti* isomer **1-r** is about 1.0 kcal/mol less stable than **1** at the G2 level. The difference in the stability of **1** and **1-r** varies between 0.8 and 1.6 kcal/mol at other levels. The S inversion path requires about 26.8 kcal/mol in **1** at the G2 level. This indicates that the S-inversion process is an unfavorable path, which is also supported by the observed increase in the S–N distance in **1-its**, as compared to **1**. We have tried to locate a transition state for the N-inversion process in **1**. The corresponding stationary point has two negative frequencies, indicating that the N-inversion in **1** is not an acceptable isomerization path between **1** and **1-r**. The S- and N-inversion paths in **1** are unfavorable because they involve filling an antibonding S–N π orbital, which is destabilizing in nature. The S–N rotational barrier in **1** at the HF/6-31+G* level is 8.92 kcal/mol. After including electron correlation at MP2(full) and the B3LYP QCISD(T) and CCSD(T) levels, the S–N rotational barrier increases to 10.12, 9.24, 9.72, and 9.72 kcal/mol, respectively. At the G2 level, the S–N rotational barrier has been estimated to be 8.51 kcal/mol, respectively. After including thermal corrections, the estimated rotational barrier is reduced to 8.50 kcal/mol (G2 free energy). All of these values are compatible to the experimentally observed rotational barrier, 9.60 kcal/mol in sulfimides.[1a]

NBO analysis suggests that there is only a sigma bond between sulfur and nitrogen in sulfimide (Table 2). The π bond is absent between sulfur and nitrogen in **1**. NBO analysis clearly indicates the presence of two lone pairs on nitrogen; one is sp^2 type (n1), and the other is pure p type (n2). The first lone-pair (n1) contributes to two weaker $n1_N \rightarrow \sigma^*_{S\text{–}H}$ negative hyperconjugative interactions ($E^{(2)}$: 6.75 kcal/mol), and the second lone-pair contributes to two stronger $n2_N \rightarrow \sigma^*_{S\text{–}H}$ negative hyperconjugative interactions ($E^{(2)}$: 22.35 kcal/mol). There is also a weak $n1_S \rightarrow \sigma^*_{N\text{–}H}$ negative hyperconjugation ($E^{(2)}$: 5.74 kcal/mol) in **1**. The above second-order interactions contribute to anomeric π bonds between sulfur and nitrogen. Apart from the negative hyperconjugative interactions, sulfimides show a back donation-type interaction from $n2_N \rightarrow$ Rydberg (3d$_{xz}$). The second-order energy associated with this interaction is 15.39 kcal/mol. During S–N rotation, the $n2_N \rightarrow \sigma^*_{S\text{–}H}$ interactions become strongly reduced, whose combined $E^{(2)}$ value reduce from 44.7 kcal/mol in **1** to 22.2 kcal/mol in **1-rts**. This reduction on anomeric π stabilization is mainly responsible for the high rotational barrier. All other S–N interactions, including $n2_N \rightarrow Ry^*_S$ marginally deviate during S–N bond rotation in **1**. From the above discussion, it can be concluded that the high S–N rotational barrier in sulfimides can be attributable to second-order negative hyperconjugative interactions, but not to the S–N pπ–pπ or dπ–pπ bond. The S–N rotational barrier in $H_2S{=}NH$, **1** is only slightly more than that of the S–N rotational barrier in HS–NH$_2$, **8** (6.66 kcal/mol). HS–NH$_2$ was also shown to posses a partial π bond due to negative hyperconjugation.[16c] It is strange to note that the S–N rotational barrier in $H_2S{=}NH$ with a formal S=N double bond is comparable to that of HS–NH$_2$, in which there is a formal S–N single bond. The substituent effect provides further clues in the analysis.

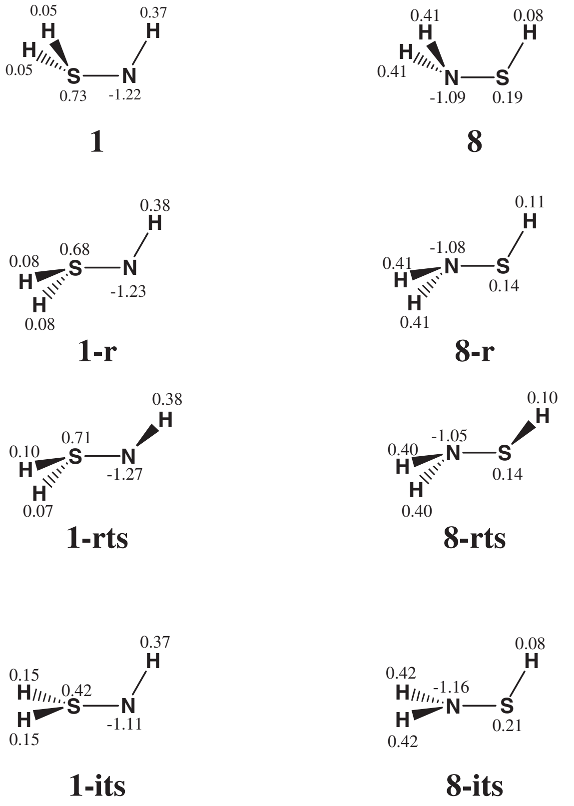


Fig. 4. The atomic charges obtained using NPA method at MP2(FULL)/6-31+G* level in **1** and **8**.

The atomic charges obtained using the NPA method and the geometries obtained at the MP2 level for **1** and **8** are given in Fig. 4. There is a strong positive charge (0.74) on sulfur, and more than a unit negative charge (−1.22) on nitrogen in **1**. The strong polarization in $H_2S{=}NH$ is in contrast to that in HS–NH$_2$, where sulfur is only weakly positive. The group charge separation across the S–N bond in $H_2S{=}NH$ is 1.69, whereas this value in HS–NH$_2$ is only 0.54. This data indicates that the semi-polar character in sulfimides is very strong. The observed smaller distance in sulfimides can be attributed to these ionic attractions in addition to negative hyperconjugation, rather than the S–N pπ–pπ strength.

Substituent Effect. Substituents cause significant changes to the rotational barriers in HS–NH$_2$, **8**. With an increase in the electronegativity of the substituent on sulfur, the S–N rotational barrier increases to very high values (from 6.6 kcal/mol in HS–NH$_2$ to 18.3 kcal/mol in FS–H$_2$N). Such a large increase in the rotational barrier has been attributed to a strong increase in negative hyperconjugative interactions in sulfimides, leading to an increase in the anomeric π strength. It is important to know whether such processes play any role in sulfimides; hence, calculations have been carried out on **2**–**7** with substitution on nitrogen (**2**–**4**) and substitution on sulfur (**5**–**7**). In sulfimides **1**–**7**, the *syn* arrangement is more stable than the *anti* arrangement. The relative thermodynamic preference for the *syn* arrangement in **1** is only ~1 kcal/mol, but in **2**–**6**, the *syn* preference is significantly high in the range

Table 3. Charge Separations Across S–N Bond in **1**–**14** Obtained from NPA Calculations

Compound	Label	Group charge	Rotamer	Rotational transition state	Inversion transition state
$H_2S{=}NH$	**1**	1.69	1.71	1.78	1.47
$H_2S{=}NF$	**2**	1.80	1.80	1.77	1.64
$H_2S{=}NHCl$	**3**	1.84	1.84	1.86	1.66
$H_2S{=}NMe$	**4**	1.72	1.76	1.84	1.52
$F_2S{=}NH$	**5**	1.42	1.45	1.54	0.59
$Cl_2S{=}NH$	**6**	1.30	1.39	1.18	1.18
$Me_2S{=}NH$	**7**	1.77	1.79	1.85	1.55
$HS–NH_2$	**8**	0.54	0.53	0.49	0.61
$HS–NF_2$	**9**	0.77	0.76	0.72	0.90
$HS–NCl_2$	**10**	0.80	0.78	0.75	0.87
$HS–NMe_2$	**11**	0.56	0.56	0.53	0.65
$FS–NH_2$	**12**	0.52	—	0.51	—
$ClS–NH_2$	**13**	0.48	—	0.46	—
$MeS–NH_2$	**14**	0.57	0.55	0.53	0.62

of 4.4–7.4 kcal/mol. In the case of **7**, the *anti* arrangement is slightly more preferred over the *syn* arrangement.

In the N substituted sulfimides **2**–**4**, two different trends have been noticed. Due to an increase in the electronegativity of on X, (in $H_2S{=}NX$), the S–N bond length increases in the order $H_2S{=}NMe$ (1.579) < $H_2S{=}NCl$ (1.607) < $H_2S{=}NF$ (1.611); the charge polarization across the S–N bond decreases in the order $H_2S{=}NMe$ (1.79) > $H_2S{=}NCl$ (1.68) > $H_2S{=}NF$ (1.21) (Table 3). The $n2_N \rightarrow \sigma^*_{S–H}$ delocalization decreases in the order $H_2S{=}NMe$ (23.58) > $H_2S{=}NCl$ (18.17) > $H_2S{=}NF$ (18.05 kcal/mol). All of these factors indicate a weakening of the S–N interaction in the same order. On the other hand, the S–N rotational barrier increases in the order $H_2S{=}NMe$ (11.98) < $H_2S{=}NCl$ (13.54) < $H_2S{=}NF$ (16.13 kcal/mol); the $E^{(2)}$ associated with $n1_S \rightarrow \sigma^*_{N–X}$ increases $H_2S{=}NMe$ (4.90) $H_2S{=}NCl$ (9.43) > $H_2S{=}NF$ (8.92 kcal/mol). These factors indicate that the S–N π strength increases with the electronegative substitution on N in sulfimides.

In the S-substituted sulfimides **5**–**7**, only one trend is observed i.e. an increase in the S–N bond strength with an increase in the electronegativity of the substituent sulfur. The S–N bond length decreases in the order $Me_2S{=}NH$ (1.588) > $Cl_2S{=}NH$ (1.511) > $F_2S{=}NH$ (1.497); the S–N rotational barrier increases in the order $Me_2S{=}NH$ (8.80) < $Cl_2S{=}NH$ (11.0) < $F_2S{=}NH$ (12.05 kcal/mol). The $n2_N \rightarrow \sigma^*_{S–X}$ delocalization strongly increases as a function of X: $E^{(2)}$ associated with this delocalization; the values are 21.46 and 60.00 kcal/mol in $Me_2S{=}NH$ and $Cl_2S{=}NH$. In $F_2S{=}NH$, an S–N $p\pi$–$p\pi$ bond has been noticed. This indicates that in the presence of highly electron withdrawing groups on sulfur, the S–N $p\pi$–$p\pi$ interaction becomes stronger. This is also evidenced by a strong S–N bond dissociation energy in $F_2S{=}NH$ (85.02 kcal/mol) in relation to that in $Me_2S{=}NH$ (36.53 kcal/mol). In the case of sulfinamide **8**–**14**, the electronegative substituents on nitrogen decrease the S–N interaction, whereas electronegative substituents on sulfur increase the S–N interaction, as indicated by trends in the S–N rotational barriers (Table 1) and second-order delocalization (Table 2).

It is intriguing to compare the properties of $H_2S{=}NH$ with $F_2S{=}NF$ and $F_2S{=}NH$. Fluorine substitution on both nitrogen and sulfur increase the S–N bond rotational barriers. In $F_2S{=}NH$, a regular $d\pi$–$p\pi$ bond has been noticed, and the $n2_N \rightarrow \sigma^*_{S–F}$ interaction becomes much weaker ($E^{(2)}$: 12.3 kcal/mol). This $d\pi$–$p\pi$ bond in $F_2S{=}NH$ is also responsible for the observed shorter S–N bond length (1.497 Å) and increased S–N rotational barriers (10.2 kcal/mol) compared to $H_2S{=}NH$. In the case of $H_2S{=}NF$, there is no $d\pi$–$p\pi$ bond, the ionic attractions are weaker, and the S–N bond length is elongated to 1.611 compared to $H_2S{=}NH$, but still showing a very high S–N bond rotational barrier (16.13 kcal/mol) due to strong negative hyperconjugative interactions. From this comparison, it is clear that an increase in the π strength from $H_2S{=}NH$ to $F_2S{=}NH$ due to the $d\pi$–$p\pi$ bond ($E_{\mathrm{rot.bar}} = 1.7$ kcal/mol) is much weaker than the increase in the π strength from $H_2S{=}NH$ to $H_2S{=}NF$ due to negative hyperconjugative interactions ($E_{\mathrm{rot.bar}} = 7.6$ kcal/mol), thus showing the importance of negative hyperconjugative interactions in sulfimides.

Conclusion

Ab initio studies on a series of sulfimides have been carried out to study their electronic structure. The S–N interactions in sulfimides are strongly ionic in nature. However, negative hyperconjugative interactions also play a significant role, as indicated by the relatively high S–N rotational barriers. Substituents strongly influence the negative hyperconjugative interactions, but weakly influence the ionic interactions across the S–N bonds in sulfimides. A comparison of S–N interactions gave better clues on the electronic structure of sulfimides. Electronegative substituents on N as well as S increase the π strength across the S–N bond.

The authors thank Council of Scientific and Industrial Research (CSIR), New Delhi for financial support.

Supporting Information

The Supporting Information contains two tables, Table 1 contains absolute energies (in a.u.) of structures **1**–**14** and related structures obtained at HF, B3LYP, MP2 (full), QCISD (T), CCSD (T), G2, and G2 Free Energy at 6-31+G* levels. Table 2 contains relative energies (in kcal/mol, ZPE values included after scaling) of the structures **1**–**14** and related structures obtained at HF, B3LYP, MP2 (full), QCISD (T), CCSD (T), G2, and G2 Free Energy at 6-31+G* levels. This material is available free of charge on the web at http://csj.jp/journals/bcsj/.

References

1 a) T. L. Gilchrist and C. J. Moody, *Chem. Rev.*, **77**, 409 (1977). b) I. V. Koval, *Sulfur Rep.*, **14**, 149 (1993). c) P. C. Taylor, *Sulfur Rep.*, **21**, 241 (1999). d) S. N. Lakeev, I. O. Maydanova, F. Z. Galin, and G. A. Tolstikov, *Russ. Chem. Rev.*, **70**, 655 (2000). e) S. Oae and N. Furukawa, “Sulfilimines and Related Derivatives,” American Chemical Society Monograph 179, Washington, DC (1987).

2 a) C. P. Baird and P. C. Taylor, *J. Chem. Soc., Chem. Commun.*, **1995**, 893. b) H. Takada, Y. Nishibayashi, K. Ohe, S. Uemura, C. P. Baird, T. J. Sparey, and P. C. Taylor, *J. Org. Chem.*, **62**, 6512 (1997). c) G. Smith, T. J. Sparey, and P. C. Tayler, *J. Chem. Soc., Perkin Trans. 1*, **1996**, 313. d) C. P. Rayner, A. J. Clark, S. M. Rooke, T. J. Sparey, and P. C. Taylor, *J. Chem. Soc., Perkin Trans. 1*, **2000**, 79. e) C. P. Baird and P. C. Taylor, *J. Chem. Soc., Perkin Trans. 1*, **1998**, 3399. f) P. S. Aujla, C. P. Baird, P. C. Taylor, H. Maugu, and Y. Vallee, *Tetrahedron Lett.*, **38**, 7453 (1997). g) C. P. Baird, A. J. Clark, S. M. Rooke, T. J. Sparey, and P. C. Taylor, *Phosphorus Sulful Silicon Relat. Elem.*, **120**, 365 (1997). h) A. J. Clark, S. Rooke, T. J. Sparey, and P. C. Taylor, *Tetrahedron Lett.*, **37**, 909 (1996). i) W. Errington, T. J. Sparey, and P. C. Taylor, *J. Chem. Soc., Perkin Trans. 2*, **1994**, 1439.

3 a) G. Celentano, S. Colonna, N. Gaggero, and C. Richelmi, *J. Chem. Soc., Chem. Commun.*, **1998**, 701. b) R. Annunziata, M. Cinquini, S. Colonna, and F. Cozzi, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 3118.

4 a) A. Armstrong, I. D. Edmonds, and M. E. Swarbrick, *Tetrahedron Lett.*, **44**, 5335 (2003). b) E. N. Suslova, A. I. Albanov, and B. A. Shainyan, *J. Organomet. Chem.*, **677**, 73 (2003). c) M. R. J. Elsegood, L. M. Gilby, K. E. Holmes, and P. F. Kelly, *Can. J. Chem.*, **80**, 1410 (2002).

5 a) R. P. Claridge, R. W. Millar, J. P. B. Sandall, and C. Thompson, *Tetrahedron*, **55**, 10243 (1999). b) R. P. Claridge, R. W. Millar, J. P. B. Sandall, and C. Thompson, *J. Chem. Res.*, **55**, 1952 (1999). c) J. P. B. Sandall, C. Thompson, and N. J. D. Steel, *J. Chem. Soc., Perkin Trans. 2*, **1997**, 513.

6 a) N. Matsumoto and M. Takahashi, *Tetrahedron*, **58**, 10073 (2002). b) N. Matsumoto and M. Takahashi, *Heterocycles*, **60**, 2677 (2003). c) J. Rabai, I. Kapovits, I. Jalsovszky, G. Argay, V. Fulop, A. Kalman, and T. Koritsanszky, *J. Mol. Struct.*, **382**, 13 (1996).

7 a) M. R. J. Elsegood, K. E. Holmes, P. F. Kelly, E. J. MacLean, J. Parr, and J. M. Stonehouse, *Eur. J. Inorg. Chem.*, **2003**, 120. b) A. V. Makarycheve-Mikhailova, N. A. Bokach, V. Yu. Kukushkin, P. F. Kelly, L. M. Gilby, M. L. Kuznetsov, K. E. Holmes, M. Haukka, J. Parr, J. M. Stonehouse, M. R. J. Elsegood, and A. J. L. Pombeiro, *Inorg. Chem.*, **42**, 301 (2003). c) M. R. J. Elsegood, K. E. Holmes, P. F. Kelly, J. Parr, and J. M. Stonehouse, *New. J. Chem.*, **26**, 202 (2002). d) K. A. N. S. Ariyaratne, R. E. Cramer, G. B. Jameson, and J. W. Gilje, *J. Organomet. Chem.*, **689**, 2029 (2004). e) M. Murakami and T. Katsuki, *Tetrahedron Lett.*, **43**, 3947 (2002). f) V. V. Thakur, N. S. C. Rameshkumar, and A. Sudalai, *Tetrahedron Lett.*, **45**, 2915 (2004).

8 a) S. Cassel, I. Plessis, H. P. Wessel, and P. Rollin, *Tetrahedron Lett.*, **39**, 8097 (1998). b) F. Chéry, S. Cassel, H. P. Wessel, and P. Rollin, *Eur. J. Org. Chem.*, **2002**, 171.

9 T. Fujii, S. Asai, T. Okada, W. Hao, H. Morita, and T. Yoshimura, *Tetrahedron Lett.*, **44**, 6203 (2003).

10 A. E. Reed and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **112**, 1434 (1990).

11 P. Politzer, G. P. Kirschenheuter, and R. S. Miller, *J. Phys. Chem.*, **92**, 1436 (1988).

12 R. F. X. Klein, P. D. N. Svoronos, V. Horak, and G. B. Jameson, *J. Org. Chem.*, **56**, 3259 (1991).

13 T. Shimizu, N. Kamigata, and S. Ikuta, *J. Chem. Soc., Perkin Trans. 2*, **1999**, 1469.

14 a) R. Haist, H. Cutin, D. C. O. Vedova, and H. Oberhammer, *J. Mol. Struct.*, **475**, 273 (1999). b) C. Leibold, R. M. S. Alvarez, E. H. Cutin, D. C. O. Vedova, and H. Oberhammer, *Inorg. Chem.*, **42**, 4071 (2003). c) F. Trautner, E. H. Cutin, C. O. D. Vedova, R. Mews, and H. Oberhammer, *Inorg. Chem.*, **39**, 4833 (2000). d) A. Hermann, M. I. M. Valdez, E. H. Cutin, D. C. O. Vedova, and H. Oberhammer, *J. Phys. Chem. A*, **107**, 7874 (2003). e) R. M. S. Alvarez, E. H. Cutin, R. M. Romano, H. G. Mack, and D. C. O. Vedova, *J. Mol. Struct.*, **443**, 155 (1998). f) R. M. S. Alvarez, E. H. Cutin, R. M. Romano, H. G. Mack, and D. C. O. Vedova, *Spectrochim. Acta, A*, **55**, 2615 (1999).

15 M. Harmata, R. Glaser, and G. S. Chen, *Tetrahedron Lett.*, **36**, 9145 (1995).

16 M. D. Burtzoff, L. Peter, P. A. Lepse, and D. Y. Zhang, *J. Mol. Struct.*, **619**, 229 (2002).

17 M. P. S. Collins and B. J. Duke, *J. Chem. Soc., Dalton Trans.*, **1978**, 277.

18 a) P. Mezey and A. Kucsman, *J. Chem. Soc., Faraday Trans. 2*, **1972**, 2060. b) P. Mezey, A. Kucsman, G. Theodorakopoulos, and G. Csizmadia, *Theor. Chim. Acta*, **38**, 115 (1975).

19 a) P. V. Bharatam, Amita, P. Uppal, and D. Kaur, *Indian J. Chem.*, **40B**, 181 (2001). b) P. V. Bharatam, P. Uppal, Amita, and D. Kaur, *J. Chem. Soc., Perkin Trans. 2*, **2000**, 43. c) P. V. Bharatam, R. Moudgil, and D. Kaur, *J. Chem. Soc., Perkin Trans. 2*, **2000**, 2469. d) P. V. Bharatam, Amita, A. Gupta, and D. Kaur, *Tetrahedron*, **58**, 1759 (2002). e) P. V. Bharatam, Amita, A. Gupta, and D. Kaur, *J. Phys. Org. Chem.*, **2002**, 197. f) P. V. Bharatam and Amita, *Tetrahedron Lett.*, **43**, 8289 (2002). g) P. V. Bharatam, Amita, and P. S. Kumar, *Bull. Chem. Soc. Jpn.*, **76**, 1911 (2003). h) P. V. Bharatam, Amita, and P. S. Kumar, *Tetrahedron*, **60**, 4801 (2004).

20 a) W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, “Ab initio Molecular Orbital Theory,” Wiley, New York (1986). b) J. B. Foresman and E. Frisch, “Exploring Chemistry with Electronic Structure Methods,” 2nd ed, Gaussian Pittsburgh, PA (1996).

21 a) R. G. Parr and W. Yang, “Density-Functional Theory of Atoms and Molecules,” Oxford University Press, New York (1989). b) L. J. Bartolotti and K. Fluchick, “In Reviews in Computational Chemistry,” ed by K. B. Lipkowitz and D. B. Boyd, VCH, New York (1996).

22 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson,

P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, "Gaussian 98W," Gaussian Inc., Pittsburgh, PA (1998).

23 P. A. Scott and L. Radom, *J. Phys. Chem.*, **100**, 16502 (1996).

24 J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.*, **87**, 5968 (1987).

25 G. D. Purvis and R. J. Barlett, *J. Chem. Phys.*, **76**, 1910 (1982).

26 L. A Curtiss, K. Raghavachari, W. G. Trucks, and J. A. Pople, *J. Chem. Phys.*, **94**, 7221 (1991).

27 A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.*, **88**, 899 (1988).