

Electronic structure of *N*-sulfonylimines

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Abstract—The electronic structure of *N*-sulfonylimines has been studied in detail using ab initio MO and density functional methods. The S–N rotational barriers in HS(O)₂N=CH₂ at G2MP2 and CBS-Q levels have been found to be 3.25 and 3.43 kcal/mol respectively. Complete optimization at HF/6-31+G*, MP2(full)/6-31+G* and B3LYP/6-31+G* levels have shown that *synperiplanar* arrangement of S–O with respect to C=N is more stable. NBO analysis has been carried out to quantitatively estimate these delocalisations and charge polarization in RS(O)₂N=CH₂ (R=H, Me, Cl, F). The Lewis basic character in *N*-sulfonylimines is less compared to *N*-alkylimines due to anomeric interactions that reduce the lone pair electron density on nitrogen in **1**. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

N-sulfonylimines (also known as sulfonimines) have been the centre of attention for organic chemists because of their ability as synthetic reagents.¹ These have been exploited for their electron deficient imine bond in inverse electron demand Diels–Alder chemistry,^{2–5} for stable and reactive alkenes in stereochemically controlled ene reactions⁶ and as valuable precursors for the preparation of *N*-sulfonyloxaziridines⁷ which have utility as chiral oxidants. The sulfaguanidine and its derivatives have been studied for their thrombin inhibitor activity and found to have moderate but intrinsically selective activity.⁸ The presence of the SO₂ group in the neighbourhood of guanidine moiety reduces its basicity providing high selectivity. Because of biological importance, the study of rotation around different bonds is essential to understand the feasible arrangement necessary for facile reactions. The S–N rotational barrier in sulfonamide⁹ **2** has been estimated to be 7–8 kcal/mol and it has been found that anomeric interactions and electrostatic interactions are responsible for the high barrier. These interactions are also expected to be important in *N*-sulfonylimines, but the presence of N=C double bond adds a new dimension. In this paper, we present the electronic structure of *N*-sulfonylimines and study the charge distribution in these systems.

2. Results and discussion

On the S–N rotational path of *N*-sulfonylimines HS(O)₂–

Keywords: *N*-sulfonylimines; *N*-alkylimines; rotational path.

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N=CH₂, three minima **1**, **1'** and **1-r**, and three rotational transition states **1-rts1**, **1-rts2** and **1-rts2'** could be located. Of the three minima, two (**1** and **1'**) are of the same energy because the two configurations have equivalent stereochemistry arising from the presence of two equivalent oxygen atoms with respect to C=N double bond. (Figs. 1 and 2). The arrangement of the C=N double bond in **1** and **1'** is *synperiplanar* with respect to the two oxygens, while in the third minimum (**1-r**) it is *synperiplanar* to S–H. The **1-r** has C_s symmetry, while **1** and **1'** have C₁ symmetry. The structural data corresponding to these structures obtained at

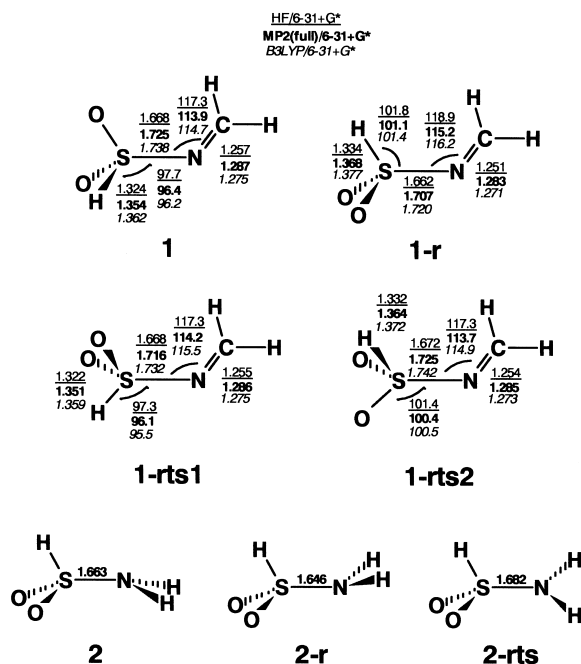


Figure 1. The important geometrical parameters and the structures of the various conformers of *N*-sulfonylimine **1** and sulfonamide **2**.

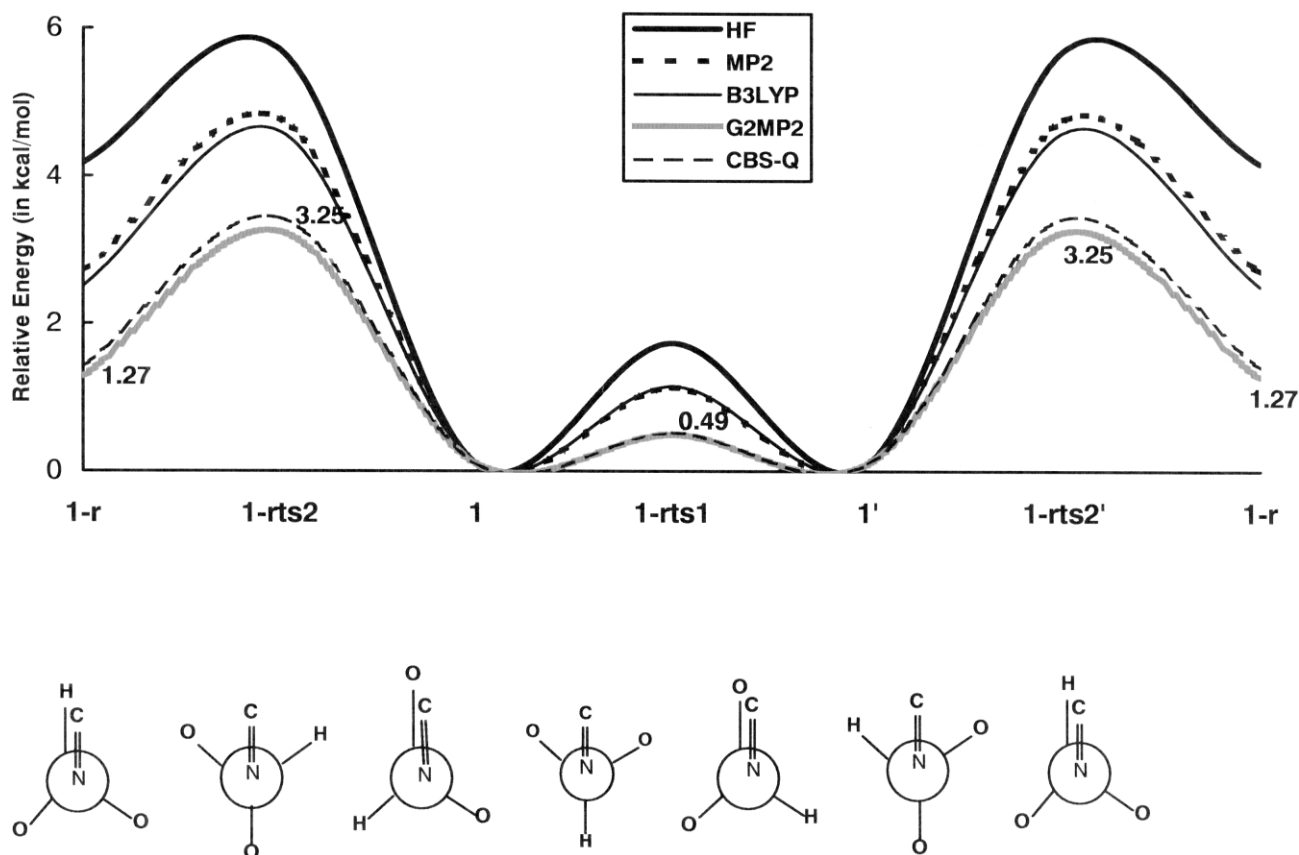


Figure 2. The potential energy surface and Newman projections of the different conformers of sulfonylimine, **1** on its S–N rotational path.

Table 1. The absolute energies (in a.u.) of the various conformers of *N*-sulfonylimine, HS(O)₂N=CH₂ at various levels

Method	1	1-r	1-rts1	1-rts2
HF/6-31+G*	-641.183504	-641.176840	-641.180746	-641.174397
MP2(full)/6-31+G*	-642.008916	-642.004596	-642.007110	-642.001298
B3LYP/6-31+G*	-643.198719	-643.194715	-643.196890	-643.191366
B3PW91/6-31+G*	-643.054081	-643.050231	-643.052135	-643.046603
CBS-Q	-642.479591	-642.477336	-642.478761	-642.994047
G2MP2	-642.446274	-642.444251	-642.445497	-642.441096

HF/6-31+G*, MP2(full)/6-31+G* and B3LYP/6-31+G* levels are given in Fig. 1. The structures **1**, **1'** are more stable relative to **1-r**. Three rotational transition states corresponding to topomerisations from **1** to **1'**, **1** to **1-r** and **1'** to **1-r** are labelled as **1-rts1**, **1-rts2** and **1-rts2'**, respectively. The structures **1-rts2** and **1-rts2'** are of the same energy. The rotational transition state **1-rts1** has an *antiperiplanar* arrangement of C=N double bond with respect to hydrogen and in **1-rts2** it is *antiperiplanar* with respect to oxygen (Fig. 2).

The S–N bond length in **1** is 1.668 Å at HF/6-31+G* level, after including the electron correlation at MP2 and B3LYP levels the bond length elongates to 1.725 and 1.738 Å (Fig. 1, Tables S1–S3), respectively. This is consistent with the earlier observation that at the electron correlated levels the S–N bond lengths are overestimated.¹⁰ The S–N bond length in **1** is longer than that in sulfonamide (**2**) (1.673 Å at MP2(full)/6-31+G* level). The S–N bond length in **1-r** is 1.707 Å at MP2(full)/6-31+G* level, which is smaller as compared to that in conformation **1** by 0.018 Å. The C=N

bond length in **1** is 1.287 Å, which is slightly longer than that in H₂C=NH (1.287 Å) at MP2(full)/6-31+G* level.

The absolute energies and relative energies of all the conformers at various levels are listed in Tables 1 and 2. The energy difference (ΔE) between the two minima (**1** and **1-r**) is 4.18 kcal/mol at HF/6-31+G* level. The ΔE between **1** and **1-r** decreases with the increase in complexity of the

Table 2. The relative energies and rotational barriers (in kcal/mol) of the various conformers of *N*-sulfonylimine, HS(O)₂N=CH₂ at various levels

Method	ΔE	S–N rotational barrier	
		1 → 1'	1' → 1-r
HF/6-31+G*	4.18	1.73	5.71
MP2(full)/6-31+G*	2.71	1.13	4.78
B3LYP/6-31+G*	2.51	1.15	4.61
B3PW91/6-31+G*	2.41	1.22	4.69
CBS-Q	1.41	0.52	3.43
G2MP2	1.27	0.49	3.25

Table 3. The various parameters of sulfonimine **1** and sulfonamide **2** at MP2(full)/6-31+G* level

Parameters	Sulfonimine (HS(O) ₂ N=CH ₂ (1))	Sulfonamide (HS(O) ₂ NH ₂ (2))
S–N bond length ^a	1.725	1.663
HSO ₂ group charge	0.258	0.290
S–N rot. barrier ^b	4.78	8.00
S–N BDE ^c	55.63	74.29
<i>Delocalisation</i> ^d		
n _O →σ _{S–N} [*]	35.92	12.20
n _O →σ _{S–H} [*]	23.06	15.84
n _N →σ _{S–H} [*]	–	4.46
n _N →σ _{S–O} [*]	6.74	2.51
<i>Orbital occupancy</i>		
ρ (n _N)	1.951	1.952
σ _{S–N} [*]	0.192	0.162
σ _{S–O} [*]	0.101	0.111

^a In Å.^b In kcal/mol.^c Bond dissociation energy in kcal/mol.^d Is second order energy for various delocalisations in kcal/mol.

quantum mechanical level. At G2MP2 and CBS-Q levels, the value is 1.27 and 1.41 kcal/mol, respectively. The rotational potential energy diagram for S–N rotation is shown in Fig. 2. The energy required for S–N rotation in **1** is 5.71 kcal/mol at HF/6-31+G* level. This value decreases slightly to 4.78 and 4.61 kcal/mol after including the electron correlation at MP2(full)/6-31+G* and B3LYP/6-31+G* levels. At the high accuracy G2MP2 and CBS-Q levels, the barrier becomes 3.25 and 3.43 kcal/mol, respectively. The S–N rotational barrier observed in **1** is much less than that observed in other systems (7–22 kcal/mol),¹¹ and is in the range of the C–C single bond rotational barrier in ethane (~3 kcal/mol).

The minima on the S–N rotational path in **1** have an *antiperiplanar* arrangement between the lone pair on nitrogen and the S–X bond (X=O in **1** and **1'** and H in **1-r**). This arrangement is favourable for negative hyperconjugative delocalisations of the lone pair electrons on nitrogen. However, the minima **1** and **1'** have eclipsed arrangement between N=C and S=O bonds, hence the overall energy gain is not substantial in **1**. The transition states on the S–N rotational path i.e. **1-rts1** and **1-rts2** have a *synperiplanar* arrangement between the lone pair of electrons on nitrogen and the S–X bond, which is less favourable for negative hyperconjugative delocalisations. Similarly in **1-rts2** the lone pair on nitrogen is in an unfavourable position with respect to the lone pair on oxygen and thus repulsive interactions cause an increase in the energy of **1-rts2**. Hence, it can be concluded that n_N→σ_{S–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.

Comparison of S–N bond interactions between **1** and **2** is of interest especially because of the observed elongation in the S–N bond length in **1** relative to **2**. The S–N bond length in **1** is 1.725 Å, which is 0.062 Å longer than that of **2**. The S–N rotational barrier (4.78 kcal/mol) and S–N bond dissociation energy (55.63 kcal/mol) in **1** are lower compared to those of **2** (8.00 and 74.29 kcal/mol, respec-

tively) at MP2(full)/6-31+G* level (Table 3). The n_N→σ_{S–O}^{*} negative hyperconjugative π strength in **1** ($E^{(2)}$ =6.74 kcal/mol) is stronger than that in **2** ($E^{(2)}$ =2.51 kcal/mol). This should have increased the S–N rotational barrier in **1** relative to **2**. NBO analysis shows that the second order energy for n_O→σ_{S–N}^{*} delocalisation ($E^{(2)}$ =35.92 kcal/mol) is almost three times stronger than that in **2** ($E^{(2)}$ =12.20 kcal/mol). This interaction increases the S–N bond length in **1**. The increased bond length reduces the anomeric π overlap and causes a reduction in the rotational barrier in **1** relative to that in **2**. The charge polarization across the S–N bond is also small in **1** (0.258e) relative to that in **2** (0.290e on HSO₂ group). Hence, the increase in n_O→σ_{S–N}^{*} interactions as well as the decrease in charge polarisation in **1** relative to that in **2** contribute towards the longer S–N bond length and weaker bond strength in **1**.

2.1. Substituents effect

The effect of substituents on S–N interactions has been studied with methyl (**3**), chlorine (**4**) and fluorine (**5**) substitution on sulfur at HF/6-31+G*, MP2(full)/6-31+G* and B3LYP/6-31+G* levels. The important geometrical parameters, relative energies, charges and orbital occupancies are given in Table 4 at MP2(full)/6-31+G* level (Fig. 3). The electron withdrawing substituents like –Cl and –F cause a decrease in S–N bond distances (0.005, 0.014 Å, respectively), while electron releasing (–CH₃) groups

Table 4. The geometrical parameters (in Å), rotational barrier (in kcal/mol), and second order delocalisation ($E^{(2)}$ in kcal/mol) in substituted sulfonimines RS(O)₂N=CH₂ at MP2(full)/6-31+G* level

Parameters	R=H (1)	R=CH ₃ (3)	R=Cl (4)	R=F (5)
S–N bond length	1.725	1.733	1.720	1.711
S–N rot. barrier	4.78	3.06	2.35	2.25
HSO ₂ group charge	0.172	0.433	0.210	0.227
<i>Delocalisation</i> ($E^{(2)}$)				
n _O →σ _{S–N} [*]	35.92	37.08	24.03	21.13
n _O →σ _{S–H} [*]	24.30	24.18	50.92	55.23
n _N →σ _{S–H} [*]	–	–	–	1.91
n _N →σ _{S–O} [*]	6.74	6.74	9.05	7.80

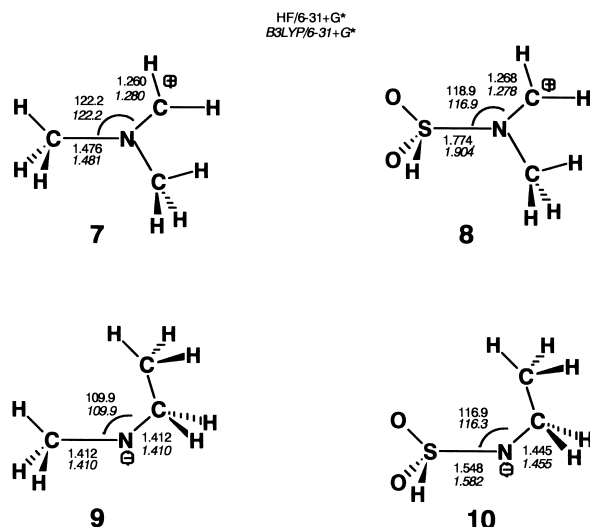


Figure 3. The important geometrical parameters and the structures of methylimine and *N*-sulfonylimine cations and anions at B3LYP/6-31+G* level.

lengthen the bond distance (0.008 Å) relative to **1**. The S–N rotational barrier in substituted *N*-sulfonylimines decreased in all the three cases and is found to be in the order **1** (4.78) > **3** (3.06) > **4** (2.35) > **5** (2.25 kcal/mol). The order is in contradiction to the bond order expected from the bond distances. The second order delocalisation energy obtained from NBO analysis at MP2(full)/6-31+G* level for $n_{\text{O}} \rightarrow \sigma_{\text{S-R}}^*$, $n_{\text{O}} \rightarrow \sigma_{\text{S-N}}^*$, $n_{\text{N}} \rightarrow \sigma_{\text{S-R}}^*$ and $n_{\text{O}} \rightarrow \sigma_{\text{S-O}}^*$ delocalisations are also given in Table 4. Chloro and fluoro substituted *N*-sulfonylimines show a decrease in $n_{\text{O}} \rightarrow \sigma_{\text{S-N}}^*$ delocalisation which also favours S–N bond length reduction. This reduction in S–N bond length is mainly due to the increase in charge polarization across the S–N bond in these systems.

2.2. Lewis acidic character of *N*-sulfonylimines

N-sulfonylimines have been reported to be electron deficient. It has also been observed that the basicity of *N*-sulfonylimines,¹ *N*-sulfonyl-1-aza-1,3-butadienes,⁷ *N*-sulfonylguanidines⁸ are less than that of corresponding alkyl systems. These experimental facts indicate that the electron density on the N as well as the C centre in the imine group is smaller in *N*-sulfonylimine compared to *N*-alkylimines. However, our charge analysis of **1** suggested that the charge separation across S–N bond is high in **1–5** and there

Table 5. The group charges and stabilization energies (in kcal/mol) due to complexation of *N*-sulfonylimine, **1** and methylimine, **6** and their cationic and anionic molecules at B3LYP/6-31+G* level

	<i>N</i> -sulfonylimine (1)	<i>N</i> -alkylimine (6)
Group charges		
N	–0.658	–0.434
–CH ₂	0.402	0.262
R ^a	0.256	0.172
E ^b	93.89	122.26
E ^c	94.27	37.99

^a R=HSO₂ (**1**) and Me (**6**).

^b Energy of stabilization due to the nucleophilic attack of imine with CH₃⁺.

^c Energy of stabilization due to the nucleophilic attack of CH₃[–] at the iminyl carbon.

is a large negative charge concentration on nitrogen in **1–5**. To quantitatively estimate the variation in the electronic distribution in alkyl and *N*-sulfonylimines, the electronic structure of **1** should be compared with that of *N*-methylimine **6** (Table 5). As expected from the experimental observations, the positive charge on the –CH₂ group in **1** is larger than that in **6**. However, the negative charge on nitrogen in **1** is also larger than that in **6**, indicating that the SO₂R substitution in imines increases the charge polarization across S–N as well as C=N bonds. To estimate the effect of this redistribution of charge on the nucleophilicity at nitrogen and electrophilicity at carbon of imines, calculations have been performed on the complexes H₂C–N(Me)₂⁺ (**7**), H₂C–N(Me)SO₂H⁺ (**8**), MeH₂C–NMe[–] (**9**) and MeH₂C–NSO₂H[–] (**10**) (Fig. 3). The energy release due to the complexation of **6** with CH₃⁺ is 122.2 kcal/mol. This value is greatly reduced in the complexation between **1** and CH₃⁺ (93.89 kcal/mol). This clearly supports the observed smaller basicity of *N*-sulfonylimines in relation to *N*-alkylimines. The extra charge at nitrogen in **1** gets localized onto the pπ orbital of N and hence does not contribute to the Lewis basic character of nitrogen. This is supported by the coefficients in the C=N π orbitals in **1** (C: 38%; N: 62%) and **6** (C: 44%; N: 56%). The anomeric delocalisation in **1** reduces the electron density from the lone pair on nitrogen and hence the Lewis basic character at nitrogen decreases, thus, though the nitrogen atom is more negatively charged in **1** relative to **6**, **1** is less basic. The nucleophilic (CH₃[–]) attack at the iminyl carbon in **6** leads to an energy release of 37.99 kcal/mol. This value is much higher in **1** (94.27 kcal/mol), suggesting the enhanced Lewis acidic character at the iminyl carbon in *N*-sulfonylimines relative to that in *N*-alkylimines.

2.3. Methods of calculations

Ab initio MO¹² and density functional (DFT)¹³ calculations have been carried out using the GAUSSIAN94W¹⁴ package, windows version of GAUSSIAN94 suite of programs. Complete optimisations have been performed on the conformations of *N*-sulfonylimine, **1**, **1-r** and its S–N bond rotational transition states **1-rts1** and **1-rts2** (Figs. 1 and 2) 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 are important.¹² To study the effect of electron correlation on the geometries and energies, full optimisations have been performed using MP2(full)/6-31+G*,¹⁵ and B3LYP/6-31+G*,¹⁶ levels also. Frequencies were computed analytically for all optimised species at 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 HF/6-31+G*, MP2(full)/6-31+G* and B3LYP/6-31+G* levels have been scaled by a factor of 0.9135, 0.9661 and 0.9806, respectively.¹⁷ The final values of S–N rotational barriers have been estimated using G2MP2¹⁸ and CBS-Q¹⁹ methods. Atomic charges in all the structures were obtained using the natural population analysis (NPA) method within the natural bond orbital approach²⁰ using MP2(full)/6-31+G* wavefunction. The substituent effect on the S–N interaction has been studied using RS(O)₂N=CH₂ (R=H, Me, Cl, F).

3. Conclusions

The S–N rotational barrier in *N*-sulfonylimines is smaller than that in sulfonamide. The S–N rotational barrier in *N*-sulfonylimines is 3.25 kcal/mol at G2MP2 level. This small barrier is responsible for the lack of any conformational preference due to S–N bond in these systems. The second order energy of $n_{\text{O}} \rightarrow \sigma_{\text{S}-\text{N}}^*$ delocalisation is responsible for the weakening of the S–N interaction in **1**. The electron withdrawing substituents on sulfur enhance the polarisation of S–N bond by increasing electron delocalisation. The electronic nature of *N*-sulfonylimine has been compared with that of *N*-alkylimine by interacting $\text{HSO}_2\text{N}=\text{CH}_2$ (**1**) and $\text{MeN}=\text{CH}_2$ (**6**) with CH_3^+ and CH_3^- . Though there is an increase in electronic charge on nitrogen in **1** compared to that in **6**, the nucleophilicity at nitrogen is smaller in **1**. The electrophilicity at carbon is higher in **1** relative to that in **6** because of the stronger charge polarization across the C=N in **1**.

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