Theoretical studies on hetero Diels–Alder reactions of sulfur diimides†

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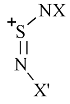
The gas-phase hetero Diels–Alder cycloaddition reactions of the sulfur diimides HN=S$^+$N$^-$X, where X = CH_3, H, Cl, CN and NO_2, with 1,3-butadiene were investigated theoretically at the B3LYP/6-31G* level. The most stable isomers of sulfur diimides have *Z,Z*-forms, which are more stable than the least stable *E,E*-forms by 6–11 kcal mol^{-1}. The reactions proceed mostly with HN=S$^+$N$^-$X (**2**) rather than HN$^-$S$^+$=NX (**2′**), even with an electron-donor X (= CH_3). The activation free energy ($\Delta G^{\ddagger}$) is lower, the stronger the electron-accepting ability of X. The lowest cycloaddition barriers are obtained in the exo-additions of the *E,E*-isomers, which are lower by *ca.* 10–13 kcal mol^{-1} than the highest barrier exo-processes of the *Z,Z*-isomers. The repulsive interactions between the diene π electrons and the endo lone pair on N (n_N), and the steric hindrance of a bulky group, are the two major factors that are responsible for the cycloaddition barrier heights.

Hetero Diels–Alder reactions provide a powerful tool for the synthesis of heterocyclic ene compounds.[1] *N*-Sulfinyl (**1**) and sulfur diimide (**2**) dienophiles with at least one electron-withdrawing group (X) on nitrogen are widely used in the preparation of dihydrothiazine oxides and imines, respectively.[1b] In a previous report,[2] we presented a density functional theory (DFT) study of the hetero Diels–Alder reactions involving *N*-sulfinyl dienophiles **1** with X = CH_3, H, Cl, CN and NO_2. It was found that although the *Z*-forms of the dienophile (**1**) are more stable than the corresponding *E*-forms, the concerted cycloaddition reactions proceed faster with the *E*-forms. The DFT calculations at the B3LYP/6-31G* level are found to predict the regio- and stereo- selectivities correctly and provide an economical way of accounting for electron correlation effects.[2–4]


1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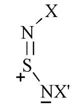
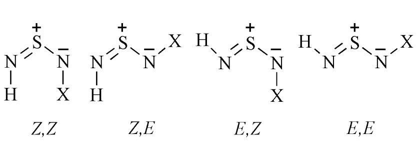

2′

In this work, we extend our DFT calculations to the hetero Diels–Alder reactions of sulfur diimide dienophiles **2** with X′ = H and X = CH_3, H, Cl, CN, and NO_2, with 1,3-butadiene at the B3LYP/6-31G* level. Due to the substituent X in **2** possible cycloaddition pathways are complex, since there are four geometric isomers, *Z,Z*, *Z,E*, *E,Z*, and *E,E* (Scheme 1) and cycloadditions can occur either at S=NH (**2**-addition) or S=NX (**2′**-addition), in addition to endo- and exo-adduct formation.


Z,Z *Z,E* *E,Z* *E,E*

Scheme 1

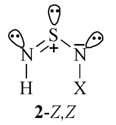
Calculations

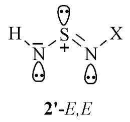
Calculations were carried out with the Gaussian 98 program.[5] Geometries of reactants, transition states and products were fully optimized at the B3LYP/6-31G* level. The stationary points were characterized by vibrational frequency calculations at the B3LYP/6-31G* level. The gas-phase B3LYP/6-31G* activation free energies, $\Delta G^{\ddagger}$, are reported relative to the separated reactants level by applying zero-point energy (ΔE_{ZPE}) and thermal energy corrections ($\Delta H^{\ddagger}$) and entropy changes ($\Delta S^{\ddagger}$) to the electronic energies ($\Delta E^{\ddagger}$). Natural bond orbital (NBO) analyses were carried out at the B3LYP/6-31G* level with the NBO-4M program[6] to determine the percentage contribution of the Lewis structures[7] corresponding to **2** and **2′**. The FMOs are obtained at the RHF/6-31G*//B3LYP/6-31G* level. In the present work, we have considered only the *concerted* cycloaddition between 1,3-butadiene and diimides.

Results and discussion

Sulfur diimides

Sulfur diimides can be represented by either Lewis structures **2** or **2′**. An electron acceptor X should stabilize **2** more than **2′**, since negative charge on N in **2** is delocalized and the structure **2** is stabilized. This expectation is indeed substantiated by the NBO analysis[6,7] of the contributing Lewis structures in Table 1. An electron donor, X = CH_3, is shown to stabilize the structure **2′** more than **2**, while for X = H the two forms contribute equally as expected.


2-*Z,Z*


2′-*E,E*

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† Electronic supplementary information (ESI) available: thermodynamic values for the *Z,Z*-forms and coordinates of the transition states. See http://www.rsc.org/suppdata/nj/b2/b204894a/

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Table 1 Percentage (%) of contributing Lewis structures at the B3LYP/6-31G* level

X	$HN{=}S^{+}N^{-}X$ (**2**)	$HN^{-}S^{+}{=}NX$ (**2′**)
CH_3	32	47
H	47	47
Cl	47	32
CN	40	30
NO_2	45	30

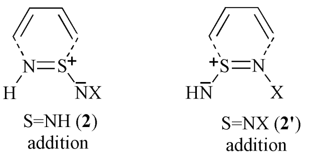
There are three sp^2 type lone pairs, one each on the N, S^+ and N^- atoms, and one p type lone pair on N^-. In the *Z*-arrangement, n_N-σ^*_{S-N} and n_S-σ^*_{N-X} (or n_S-σ^*_{N-H}) vicinal charge transfer stabilization interactions are expected to be stronger than in the corresponding *E*-arrangement, since in the *Z*-form the interacting orbitals, *n* and σ^*, are antiperiplanar whereas in the *E*-form they are synperiplanar.[8] Thus the *Z,Z*-form is the most stable while the *E,E*-form is the least stable (Table 2). As the X becomes a stronger electron acceptor, the *Z,E*-form becomes more stable than the *E,Z*-form due to the stronger antiperiplanar n_N-σ^*_{S-N} interaction in the *Z,E*-form than the synperiplanar n_N-σ^*_{S-N} interaction in the *E,Z*-form for the Lewis structure **2**. It is interesting to note in Table 2 that one conversion of *Z* to *E* costs *ca.* 1.3 kcal mol^{-1} (from *Z,Z* to *Z,E* or *E,Z*) but two simultaneous conversions (from *Z,Z* to *E,E*) cost *ca.* 6.1 kcal mol^{-1}, which is more than two times the additive effect ($1.3 + 1.3 = 2.6$). This may result from a larger *n-n* repulsive interaction in the antiperiplanar than the synperiplanar *n-n* arrangement.[8] It should be noted that the addition of a diffuse function (B3LYP/6-31+G*) does not change the trends of relative stabilities (Table 2).

Experimentally, the mixed forms, *Z,E* and *E,Z*, are found to be more abundant than the symmetrical isomer (*Z,Z*).[1b,9] Albeit stabilities of the *Z,E*- and *E,Z*-forms are lower than that of the most stable form, *Z,Z*, the differences, $\Delta G = G(E,Z$ or $Z,E) - G(Z,Z)$, are small so that the two mixed forms may exist in larger amounts than the most stable form (*Z,Z*) at low temperature, as ^1H- and ^{13}C-NMR spectroscopy in solution indicated.[1b] Rotational barriers around the S–N bond are rather high, at 14.8–21.2 and 17.7–22.5 kcal mol^{-1} for $X = CH_3$ and NO_2 respectively. This means that configurational equilibrium can take place only at high temperature. Such inter-conversions between different isomers were observed by coalescence of the ^1H-NMR signals at higher temperatures.[1b]

Table 2 Comparison of the stabilities, ΔE_{ZPE} (ΔG), of the four forms of sulfur diimide dienophiles (kcal mol^{-1})

X	*Z,Z*	*E,Z*	*Z,E*	*E,E*
CH_3	0.0	1.2[a]	3.1	8.1
		1.6[b]	3.5	8.6
		0.5[c]	3.0	7.4
H	0.0	1.3	1.3	6.1
		1.3	1.3	6.1
		0.4	0.4	4.6
Cl	0.0	4.1	5.3	11.2
		4.1	5.2	11.0
		3.5	7.9	10.2
CN	0.0	4.6	3.2	7.9
		4.7	3.3	8.1
		4.1	3.1	7.3
NO_2	0.0	7.3	3.1	8.1
		7.0	3.1	8.0
		6.0	2.7	7.6

[a,b] Relative ΔE_{ZPE} and ΔG values, respectively, at the B3LYP/6-31G* level. [c] Relative ΔG values at the B3LYP/6-31G* level. Absolute values for the *Z,Z* forms are collected in Table S1 in the Electronic supplementary information (ESI).



Scheme 2

S=NH (2) *vs.* S=NX (2′) cycloaddition

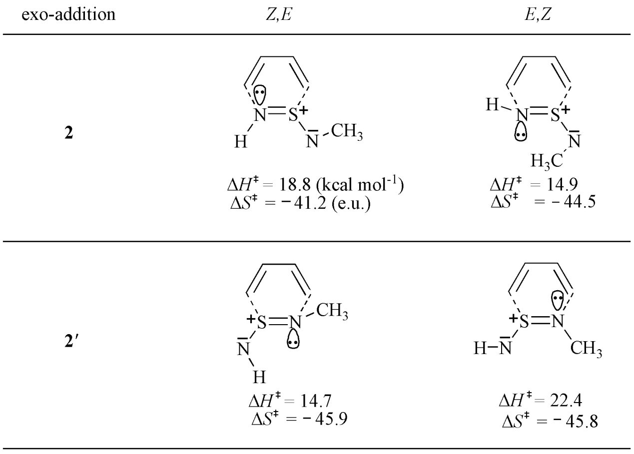
The sulfur diimide can add to a diene either at the S=NH (**2**) or S=NX (**2′**) moieties, Scheme 2. Although percentage contributions of the S=NH (**2**) structures are higher than the S=NX (**2′**) forms for electron acceptor X (Table 1), we nevertheless calculated the activation barriers ($\Delta G^{\ddagger}$) for the cycloaddition of diimides with $X = CH_3$ and NO_2 for both **2** and **2′** structures, as shown in Table 3. Examination of this table shows that all except one case, *Z,E*-exo-addition of $X = CH_3$, the **2′** addition exhibits a higher activation barrier, irrespective of having an electron donor ($X = CH_3$) or acceptor ($X = NO_2$) substituent.

There are two dominant factors that elevate barrier heights ($\delta\Delta G^{\ddagger} > 0$) in the concerted cycloaddition transition state (TS): (*i*) the lone pair orbital on N, which can interact repulsively with the π-electrons of the diene, raising the activation energy ($\delta\Delta H^{\ddagger} > 0$), and (*ii*) steric hindrance of a bulky substituent, such as $X = CH_3$, in the TS; the effect will be reflected in the lower entropy of activation ($\delta\Delta S^{\ddagger} < 0$). For example, let us examine the TS structures involved in the exo-additions of the *Z,E*- and *E,Z*-forms with $X = CH_3$ shown in Scheme 3

Table 3 Comparison of $\Delta G^{\ddagger}$ (kcal mol^{-1}) values for S=NH (**2**) *vs.* S=NX (**2′**) cycloaddition at the B3LYP/6-31G* level

Path	X	*E,E*	*Z,E*	*E,Z*	*Z,Z*
Endo	CH_3	23.58	26.81	31.22	31.39
		(24.63)[a]	(28.34)	(32.69)	(34.69)
	H	23.90	27.03	26.94	29.49
	NO_2	14.78	15.69	20.88	19.32
		(22.42)	(25.16)	(25.09)	(30.45)
Exo	CH_3	22.75	31.11	28.22	34.66
		(25.41)	(28.43)	(36.09)	(37.88)
	H	22.15	30.97	25.57	33.45
	NO_2	12.32	19.29	18.45	22.50
		(20.48)	(23.66)	(29.48)	(32.89)

[a] Values in parentheses are for the S=NX (**2′**) addition.



Scheme 3

Table 4 Frontier molecular orbital levels (a.u.) calculated at the HF/6-31G*//B3LYP/6-31G* level

	Normal electron demand			Reverse electron demand		
X	Diene HOMO	Dienophile LUMO	$\Delta\varepsilon_{FMO}$	Dienophile HOMO	Diene LUMO	$\Delta\varepsilon_{FMO}$
CH_3	−0.3223	0.0528	0.38	−0.3605	0.1272	0.49
H	−0.3223	0.0508	0.37	−0.3801	0.1272	0.51
Cl	−0.3223	0.0223	0.34	−0.3819	0.1272	0.51
CN	−0.3223	−0.0159	0.31	−0.3943	0.1272	0.52
NO_2	−0.3223	−0.0208	0.30	−0.4772	0.1272	0.60

(data in Table S2 in the ESI). We note that the endo lone pair on N raises the $\Delta H^\ddagger$ value whereas the endo CH_3 group lowers the $\Delta S^\ddagger$ value. For *E,Z*-exo-addition the difference in $\Delta S^\ddagger$ is small since in **2** there is a sterically unfavorable endo H while in **2′** there is a proximate bulky CH_3 group. For the *Z,E*-exo with **2′** the energy is lower by 4.1 kcal mol^{-1} ($\delta\Delta H^\ddagger < 0$), which more than compensates for the lower entropy of activation by 4.7 e.u. ($-T\Delta S^\ddagger = +1.4$ kcal mol^{-1} at 298 K). This is why the *Z,E*-**2′** addition of X = CH_3 has a lower activation barrier than the corresponding *Z,E*-**2** addition. The bulky CH_3 group attached directly to the bond-making N atom in **2′** addition leads to a sterically unfavorable TS structure and causes a lower activation entropy (and hence raises the activation barrier).

Another important factor that leads to **2** rather than **2′** addition is that the p_π lobe size on N(H) is always larger than that on N(X) when X is an electron acceptor (*vide infra*). It should be stressed that the **2** form of sulfur diimides with an electron-withdrawing group X is not only more stable and hence more abundant but also leads to a lower barrier path in the hetero Diels–Alder cycloaddition than the **2′** form, and this is in accord with the ample experimental results reported in the literature.[1b]

For X = H there is no difference between **2** and **2′** addition since the diimide is symmetrical. Since the *Z,E*-exo-**2′** addition of X = CH_3 is the only exceptional case where **2′** leads to a lower activation barrier than **2**, we discuss the **2** additions only in the following.

The relative reactivities

Examination of the frontier molecular orbitals (FMOs) in Table 4 reveals that the present reactions are normal electron demand Diels–Alder cycloadditions through interaction between diene HOMO and dienophile LUMO. The charge transfer interaction energies, eqn. (1),

$$\Delta E^{(2)}{}_{\pi-\pi^*} = -\frac{2F^2_{\pi\pi^*}}{\varepsilon_{\pi^*} - \varepsilon_\pi} \qquad (1)$$

should be the greater, the narrower the FMO gap, $\Delta\varepsilon = \varepsilon_{\pi^*} - \varepsilon_\pi$, and the greater the overlap between the two orbitals ($F_{\pi\pi^*} \propto S_{\pi\pi^*}$).[7a,10] The FMO gap decreases (Table 4) and the lobe size ($S_{\pi\pi^*} \propto p_\pi$ AO coefficient) grows larger (Table 5) on the N(H) atom as the electron-withdrawing power of substituent X gets stronger, so that the charge transfer from the diene toward the sulfur diimide dienophile in the TS becomes stronger and consequently the activation barrier becomes lower. It is also to be noted that the reaction becomes more exothermic with the increase in electron-accepting power of X, for example in the *Z,Z*-exo addition, $\Delta E^\circ = -12.0$ (X = CH_3), −14.5 (H), −19.6 (Cl), −22.2 (CN), and −29.2 (NO_2) kcal mol^{-1}. Thus, the concerted cycloaddition with a stronger electron acceptor X is favored kinetically as well as thermodynamically. In Table 5 we note that the p_π lobe size on the N(H) atom grows but that on the N(X) atom shrinks with the increase in the electron-accepting power of X. This provides one factor that is responsible for the preference of **2**-addition over **2′**-addition as mentioned above.

Table 5 The p_π AO coefficients of HN1–S2–N3X calculated at the HF/6-31G*//B3LYP/6-31G* level

X	N1 ($2p_z + 3p_z$)	S2 ($3p_z + 4p_z$)	N3 ($2p_z + 3p_z$)
CH_3	−0.75	1.03	−0.75
H	−0.76	1.07	−0.76
Cl	−0.79	1.03	−0.73
CN	−0.81	1.00	−0.54
NO_2	−0.83	0.96	−0.44

The trend of lower activation barrier for the dienophile with a stronger electron acceptor X is evident in Table 6 where we have summarized the activation energies, $\Delta G^\ddagger$. Other notable trends are: (*i*) the *E,E*-form leads to a lower barrier for the cycloaddition than the *Z,Z*-form, which is in contrast to the more stable *Z,Z*-form of sulfur diimides than the *E,E*-form, and (*ii*) the endo-additions have higher activation barriers than the exo-additions for the *E,E*- and *E,Z*- isomers, in contrast the reverse hold for the additions of *Z,Z*- and *Z,E*- isomers. The representative TS structures are shown in Fig. 1 for X = CH_3. We note that the TSs are all asynchronous, that is the C–N bond making is more advanced than C–S bond formation, and the *Z,Z*-isomer forms a somewhat later TS along the reaction coordinate than the *E,E*-isomer with more advanced formation of the C–N and C–S bonds in the TS. The closer approach of the two reactants with *Z,Z*- than *E,E*-isomers appears to lead to a greater exclusion repulsion so that barrier heights become higher.[10] The extent of bond formation, as expressed by the percentage bond order change, $\%\Delta n^\ddagger$ given by eqn. (2),[11] in the TS are shown in Table S3 (ESI).

$$\%\Delta n^{\neq} = \frac{[\exp(-r^{\neq}/a) - \exp(-r_R/a)]}{[\exp(-r_P/a) - \exp(-r_R/a)]} \times 100 \qquad (2)$$

In eqn. (2), $r^\ddagger$, r_P and r_R are the bond lengths in the TS, product and reactant, respectively, and $a = 0.6$. Since $r_R = \infty$ for C–N and C–S bonds in the reactant, the second exponential terms vanish: $\exp(-r_R/a) = 0$.

Table 6 Free energies of activation, $\Delta G^\ddagger$ (kcal mol^{-1}), for gas-phase cycloaddition of sulfur diimides with *cis*-1,3-butadiene at the B3LPY/6-31G* level

Path	X	*E,E*	*Z,E*	*E,Z*	*Z,Z*
endo	CH_3	23.58	26.81	31.22	31.39
	H	23.90	27.03	26.94	29.49
	Cl	19.45	22.21	28.20	29.28
	CN	17.61	19.37	21.56	21.44
	NO_2	14.78	15.69	20.88	19.32
exo	CH_3	22.75	31.11	28.22	34.66
	H	22.15	30.97	25.57	33.45
	Cl	18.69	27.00	24.99	31.88
	CN	15.51	23.19	18.43	24.78
	NO_2	12.32	19.29	18.45	22.50

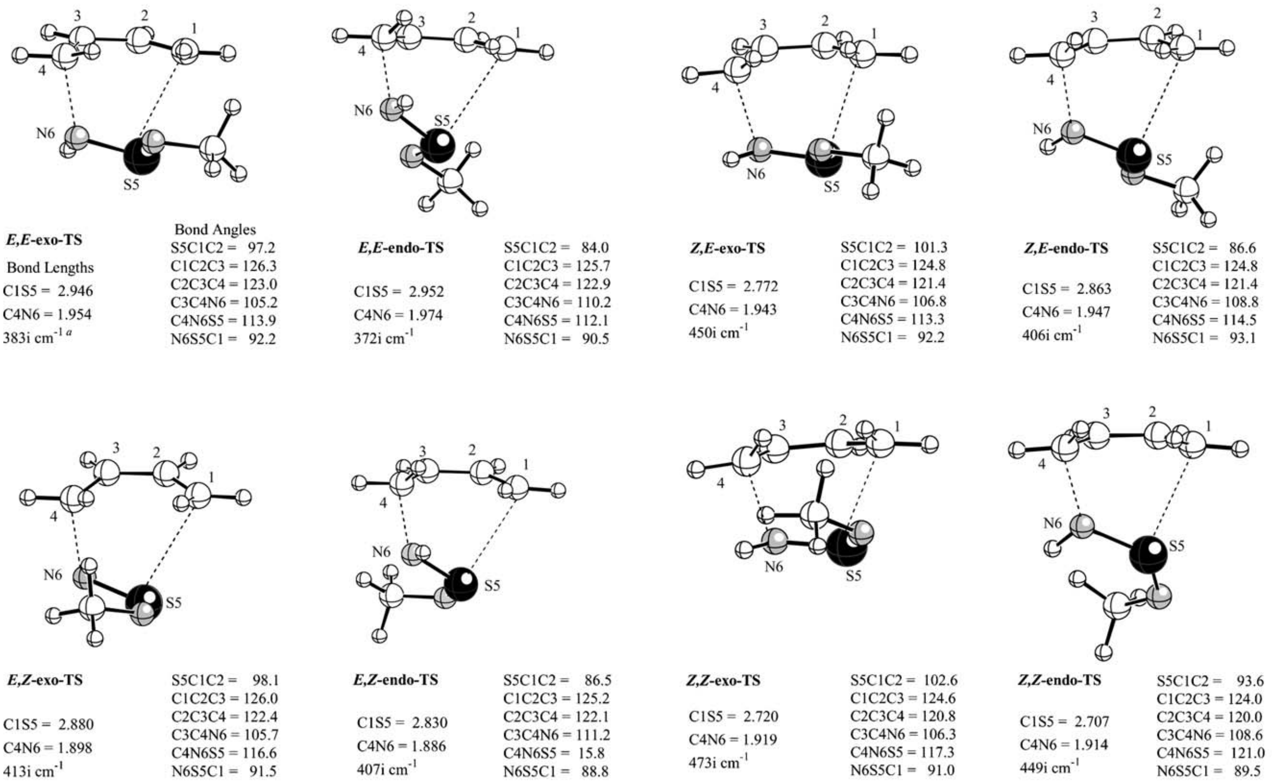


Fig. 1 TS structures for cycloadditions of sulfur diimides to 1,3-butadiene with X = CH_3. Bond lengths are in Å and angles are in degrees. *a* Negative eigenvalue in the Hessian matrix.

In general, bond formations in the TS are asynchronous with C–N bond formation exceeding C–S bond making by more than 20%. The concerted cycloaddition becomes more synchronous as the electron-withdrawing power of X increases ($X = CH_3 \rightarrow H \rightarrow NO_2$). For example in the *E,E*-exo-addition, the difference in the $\%\Delta n^\ddagger$ value between the C–N and C–S bonds decreases as $\delta(\%\Delta n^\ddagger) = [\%\Delta n^\ddagger(\text{C–N}) - \%\Delta n^\ddagger(\text{C–S})] = 28.6\ (X = CH_3) \rightarrow 26.0\ (X = H) \rightarrow 7.4\%\ (X = NO_2)$. Since the reaction barrier decreases with the increase in the electron-accepting power of X, this means that the reaction proceeds more readily in the more synchronized bond formation in the TS.

For the *Z,Z*-exo- and *E,E*-endo-additions, the sp^2 lone pair on N (n_N) is directed toward the diene so that the repulsive interaction between n_N and the π-electrons of the diene should be large and the barrier height is larger than that in the corresponding *Z,Z*-endo- and *E,E*-exo-additions. Likewise, in the *E,Z*-endo- and *Z,E*-exo-additions the n_N has an endo arrangement so that barrier heights are greater than those in the corresponding *Z,E*-endo- and *E,Z*-exo-additions for which the n_N has an exo-arrangement. The barrier height differences between the *E,E*- and *Z,Z*-isomers $[\delta\Delta G^\ddagger = \Delta G^\ddagger(Z,Z) - \Delta G^\ddagger(E,E)]$ are smaller for endo- (4.5–9.8 kcal mol^{-1}) than exo-addition (9.3–13.2 kcal mol^{-1}), reflecting rather large steric effects involved in all of the endo-additions. These latter barrier height differences ($\delta\Delta G^\ddagger$) in the exo-additions are, however, somewhat greater than the energy difference between the sulfur diimide isomers $[\delta G^\circ = G^\circ(E,E) - G^\circ(Z,Z) = 6\text{–}11\ \text{kcal mol}^{-1}]$. This means that the *E,E*-exo-**2**-type addition may constitute the major pathway for the 1,3-butadiene-sulfur diimide hetero Diels–Alder cycloaddition. The *E,E-endo*-**2**-type additions have barrier heights higher by 0.8–2.5 kcal mol^{-1} than the lowest *E,E-exo*-pathway so that both exo- and endo-additions of the *E,E*-isomer may proceed competitively.

Conclusion

The most stable isomer of sulfur diimide has a *Z,Z*-form that is more stable by 6–11 kcal mol^{-1} than the least stable *E,E*-form. Of the two formal Lewis structures of the sulfur diimides, $HN{=}S^+N^-X$ (**2**) and $HN^-S^+{=}NX$ (**2′**), the former (**2**) contributes more than the latter for an electron-acceptor X. The hetero Diels–Alder cycloaddition occurs, however, mostly with the **2** form, even with an electron-donor X ($= CH_3$). The cycloaddition barrier is lower, the stronger the electron-accepting power of X ($= NO_2$). The lowest cycloaddition barriers are exhibited in the exo-additions of the *E,E*-isomers, which are lower by *ca.* 10–13 kcal mol^{-1} than the highest barrier exo-processes of the *Z,Z*-isomers. The two factors that are important in determining the barrier height ($\Delta G^\ddagger$) are (*i*) the sp^2 type lone pair on N(H), n_N, which elevates the activation energy ($\delta\Delta H^\ddagger > 0$) when directed in an endo fashion and (*ii*) the steric hindrance of a bulky substituent X, which increases the negative entropy of activation ($-\Delta S^\ddagger > 0$).

Acknowledgements

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