

Theoretical Investigation on the Reactivity of Sulfur-Centered Heterocumulenes as Dienophiles in Diels–Alder Reactions and Endo-Lone-Pair Effect

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ABSTRACT: AM1 and PM3 computations show that thiocarbonyl S-oxide and thiocarbonyl S,S-Dioxide undergo Diels–Alder cycloadditions with cyclopentadiene and anthracene to form thiabicyclic adducts through asynchronous transition structures (TSs) with C=S π^* involving in the reaction at a very early stage. Calculated activation barriers indicate that the dienophilicity of these heterocumulenes decrease gradually with progressive addition of oxygen atom on thiocarbonyl sulfur, in reasonable agreement with experimental observations. Frontier Molecular Orbital (FMO) and deformation energy analyses reveal that the above trend is due to gradual destabilization of lowest unoccupied molecular orbital (LUMO) of the dienophile and increase of deformation energy of both diene and dienophile with increase of oxygen atoms around sulfur. Analysis of bond orders and TS geometries show that the TSs are neither “early” nor “late.” Chlorine substitution on these heterocumulenes does not seem to increase their reactivity contrary to expectations. The reactions of monosubstituted sulfines with cyclopentadiene pass through four very closely lying TSs and stereoselectively form four stereoisomeric products. For the above reason, the computed barriers show a mixed trend although the relative exothermicity of these reactions are in order. © 1998 John Wiley & Sons, Inc. *Int J Quant Chem* 66: 309–322, 1998

Key words: Sulfine; sulfene; Diels–Alder reaction; semiempirical method; AM1; PM3; transition structure

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Introduction

Heterocumulenes offer very interesting systems for studying heteroatomic influence on reactivity of the cumulenic systems in cycloadditions [1a]. Of all the heterocumulenes, thiocarbonyl S-oxide and thiocarbonyl S,S-dioxide are the least investigated, and this is due to the fact that they are highly reactive species and can only be generated in situ and entrapped by further reactions [1, 2]. Thiocarbonyl S-oxide and thiocarbonyl S,S-dioxide compounds, also known as sulfines and sulfenes, respectively, are synthetically useful reagents in various organic reactions [1, 2] and are interesting partners in cycloaddition reactions [3–7]. Diels–Alder reactions of these thiocarbonyls with various dienes, viz. 2,3-dimethylbutadiene, cyclopentadiene, anthracene, etc., have been the subject of several experimental reports [3–8] and significant progress has been made in understanding their dienophilicity and stereochemical outcome of their reactions. Experimental reports [1–8] reveal that sulfines and sulfenes are electrophilic in nature, with reactions occurring preferentially at C—S π bond over S—O π bond in Diels–Alder processes. Monosubstituted sulfines are of special interest in that they are nonlinear heterocumulenes and can exist as Z or E isomers, and therefore can form stereoselective products on reacting with dienes [5–7].

All-carbon Diels–Alder [9] and hetero Diels–Alder [10–15] reactions have been studied extensively at different levels of theory. Although numerous theoretical and mechanistic investigations have been made on the (2 + 2) [16–19] and (4 + 2) [20] cycloadditions of various heterocumulenes, viz. ketene, ketenimine, isocyanate, etc., the investigations on the Diels–Alder reaction of sulfines and sulfenes are very rare. A few molecular orbital studies [21] on them show that these heterodienophiles are configurationally sufficiently stable molecules and chemically reactive in cycloadditions. Here, we investigate the mechanism of a set of Diels–Alder reactions involving sulfines and sulfenes with certain dienes using semiempirical molecular orbital (MO) models through location of transition structures (TS), and the following questions are addressed in this work: (i) the effect of various thiocarbonyl environment on the kinetic and thermodynamic control of the reactions in-

volving $R_2C=SO_n$ ($n = 0-2$) as dienophiles, (ii) the effect of chlorine substitution on the dienophilicity of these heterocumulenes, and (iii) the stereoselectivity in reactions involving some monosubstituted sulfines ($RHC=SO$) and endolone-pair effect in such heterocumulene reactions. Specifically, Diels–Alder reactions of thioformaldehyde S-oxide and thioformaldehyde S,S-dioxide, and their thiophosgene analogs with cyclopentadiene and anthracene have been investigated. The reactions of these two dienes with thioformaldehyde and thiophosgene have also been studied for comparison. The Z/E isomers of a set of monosubstituted sulfines, viz. chloro, methyl, and trifluoromethyl sulfines, have been chosen as model systems to react with cyclopentadiene to observe stereoselectivity in these reactions, and it is to be noted that these sulfines are thermally labile in Diels–Alder processes [7, 8].

Method of Computation

The semiempirical molecular orbital calculations have been performed with AM1 and PM3 Hamiltonians [22] using the MOPAC 6.0 [23] program implemented in Micro Vax II and in Silicon Graphics IRIS workstation. Reactant and product geometries have been fully optimized using Baker's eigenvector following (EF) procedure [24]. The gradient norm computed in this routine is significantly better than that obtained using the BFGS procedure. The saddle point geometries (TSs) were optimized and refined using the same routine with TS, DMAX = n.nn, and RECALC = n options. Though the EF routine confirmed the saddle point as first-order TS, the force calculations were performed to check if the eigenvectors associated with the single imaginary frequency in the diagonalized Hessian matrix corresponded to the reaction coordinate. TSs formed in the reaction between cyclopentadiene and thioformaldehyde/sulfine/sulfene are noted as CS1–CS20 (Figs. 2 and 5) and correspondingly those formed in the reaction between anthracene and thiocarbonyl/sulfine/sulfene are noted as AS1–AS6 (Fig. 3). The energy required for deformation of diene and dienophile at TS has been calculated as discussed earlier [25a]. Further, ab initio lowest unoccupied molecular orbital (LUMO) energies of the chosen heterodienophiles have been computed at HF/6-31G*

level using GAUSSIAN 94W [26] with RFO (rational function optimization) option available in berny algorithm.

Bond order analysis of various bonds that play a dominant role in the reactions is done as follows. In the Diels–Alder cycloaddition, some bonds are formed and some other undergo cleavage. The extent of bond formation/bond cleavage of a specific bond i at the TS can be calculated [27] as

$$BF_i \text{ or } BC_i = \frac{BO_i^{\text{TS}} - BO_i^{\text{R}}}{BO_i^{\text{P}} - BO_i^{\text{R}}} \times 100$$

where BO_i^{TS} , BO_i^{R} , and BO_i^{P} are the bond order values of the specific bond i that is forming or cleaving during reaction, at the TS, reactant and product, respectively. This would clearly indicate the extent of involvement of that bond in the reaction. Further, from the percentages of bond formation and cleavage of all the bonds involved in the reaction, average bond forming/cleaving at the TS can be calculated as

$$BF_{\text{Ave}} = \frac{1}{n_i} \sum_i \text{forming bonds } BF_i$$

$$BC_{\text{Ave}} = \frac{1}{n_j} \sum_j \text{cleaving bonds } BC_j$$

$$BFC_{\text{Ave}} = \frac{1}{2} (BF_{\text{Ave}} + BC_{\text{Ave}})$$

The BF_{Ave} and BC_{Ave} show the extent of average bond formation and average bond cleavage at the TS, and from these one can infer the relative domination of bond making and breaking processes at the TS. BFC_{Ave} gives the average percentage of all bond making and cleaving processes at the TS. This value seems to indicate the “earliness” or “lateness” of TS in the reaction.

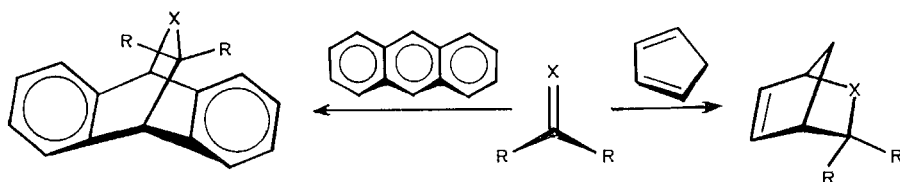
Results and Discussion

The reactions investigated here are drawn in Figure 1 in which type A presents the reactions of various thioformaldehydes (1–3) and thiophosgenes (4–6) with cyclopentadiene and anthracene, and type B presents those of monosubstituted sulfines (7–9) with cyclopentadiene. Computed AM1, PM3, and HF/6-31G* LUMO energies and the charges on C and S of the above hetero-

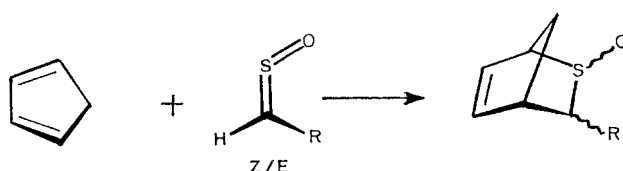
dienophiles are also presented in Figure 1. The HF/6-31G* LUMO values have been calculated to check the trend in AM1 (PM3) values, and this is due to the earlier report that FMO analysis based on semiempirical results [25] are sometimes unreliable. Computed TSs for reactions involving the dienophiles 1–6 (type A) are shown in Figures 2 and 3. Figure 4 presents a sketch of the barrier connecting the reactant, TS, and product states that are plotted on the relative energy versus BFC_{Ave} values. Relative energies of TS and product states are with reference to the reactant state. The graph is representative in that only AM1 values have been taken and the graph is drawn for a limited set of reactions. The graph visually conveys the relative positioning of product and TS states for a set of closely related reactions. Reactions of 2 and 5 with cyclopentadiene can proceed through *exo/endo* selective TSs while no such twin approach is possible in anthracene reactions, and this is in view of the symmetry of anthracene. Figure 5 contains the TSs for the various stereoselective reactions (type B) involving monosubstituted sulfines (7–9) with cyclopentadiene. The newly forming and cleaving dienophile bonds are presented in their respective TSs (Figs. 2–5). The glide angles θ_1 and θ_2 and the twist angle ϕ are presented in Table I. The degree of asynchronicity (α) is also presented in the table. Frontier orbital energy (FOE) gaps, quantum of charge transfer (q_{CT}), activation and reaction energies, and deformation energy of both reactants at the TS for type A reactions are collected in Table II. Those for type B reactions are given in Table IV. Calculated percentage of bond make–break at the TS for the type A reactions are summarized in Table III.

REACTIONS OF $R_2C=S$, $R_2C=SO$, AND $R_2C=SO_2$ WITH CYCLOPENTADIENE AND ANTHRACENE

Thiocarbonyl compounds are known to be more efficient dienophiles than their corresponding carbonyl compounds. This is due to the fact that thiocarbonyl bond is weaker than carbonyl bond, and further less bond strain is involved during the formation of TS [11]. Sulfines and sulfenes are the functional derivatives of thiocarbonyl and are known to act as efficient heterodienophiles [1–8]. These reactions have been observed [2, 3] to be concerted cycloaddition processes and are LUMO dienophile controlled. The LUMOs in both sulfines and sulfenes are found to be $C=S \pi^*$ orbitals. The



	X	R	LUMO (eV)	Charge	
				C	S
1	CH ₂	H	0.386(0.443)[5.006]	-0.290(-0.154)[-0.381]	0.074(0.007)[0.056]
2	S	H	-0.821(-1.436)[1.540]	-0.897(-1.229)[-0.589]	1.297(0.978)[0.795]
3	SO ₂	H	0.263(-0.109)[2.748]	-1.483(-1.121)[-0.703]	2.835(2.331)[1.355]
4	S	Cl	-1.686(-2.049)[0.680]	-0.180(-0.281)[-0.245]	0.164(0.011)[0.047]
5	SO	Cl	-1.305(-1.828)[0.871]	-0.695(-0.673)[-0.407]	1.281(0.919)[0.857]
6	SO ₂	Cl	-0.693(-0.731)[1.905]	-1.226(-1.122)[-0.520]	2.780(2.320)[1.419]



	R		LUMO (eV)	Charge	
				C	S
7	Cl	Z	-0.852(-1.534)[1.361]	-0.793(-0.638)[-0.483]	1.278(0.930)[0.820]
		E	-0.927(-1.603)[1.197]	-0.792(-0.631)[-0.477]	1.286(0.944)[0.833]
8	Me	Z	-0.480(-1.252)[2.095]	-0.784(-0.536)[-0.383]	1.244(0.918)[0.758]
		E	-0.503(-1.282)[2.041]	-0.795(-0.546)[-0.371]	1.254(0.926)[0.753]
9	CF ₃	Z	-1.354(-2.126)[1.034]	-0.944(-0.720)[-0.590]	1.421(1.094)[0.851]
		E	-1.402(-2.189)[0.925]	-0.948(-0.721)[-0.562]	1.427(1.095)[0.864]

FIGURE 1. Scheme of the reactions with AM1 (PM3) [HF / 6-31G*] LUMO energies and charges on C and S.

FOE gaps and q_{CT} values presented in Table II for the set of reactions mentioned as type A in Figure 1 reveal that these reactions are normal electron demand hetero Diels–Alder reactions and positive q_{CT} values obtained is a clear indication of that.

Transition State Geometry

Sulfines and sulfenes are the bent heterocumulenes, and they are found to undergo (4 + 2) cycloadditions with cyclopentadiene and anthracene through asynchronous thiacyclic TS in a concerted way. Owing to the unsymmetrical nature of these heterodienophiles and the differently maturing C₄ ⋯ S₅ and C₆ ⋯ C₁ new σ bonds, the TSs are asynchronous. This is quite evident from the calculated α (degree of asynchronicity) values listed in

Table I. The asynchronicity at the TS is more pronounced in all thiophosgene (4–6) reactions compared to simple thioformaldehyde (1–3) reactions. These heterodienophiles—thiocarbonyls (1 and 4), sulfines (2 and 5), and sulfenes (3 and 6)—have been shown above as electrophilic in nature, and in the two reactive sites sulfur is found to be more electrophilic than the carbon site as can be seen from the charges of both atoms (Fig. 1). Therefore, the sulfur should react first, and naturally the rate of maturation of the newly forming C—S bond should be greater than that of C—C bond. This can be seen from the calculated percentage of bond formation at the TS presented in Table III for the c₄ ⋯ S₅ and C₆ ⋯ C₁ bonds. The same trend can also be seen from the computed C₄ ⋯ S₅ and C₆ ⋯ C₁ bonds at the TS (Figs. 2 and 3). The percent-

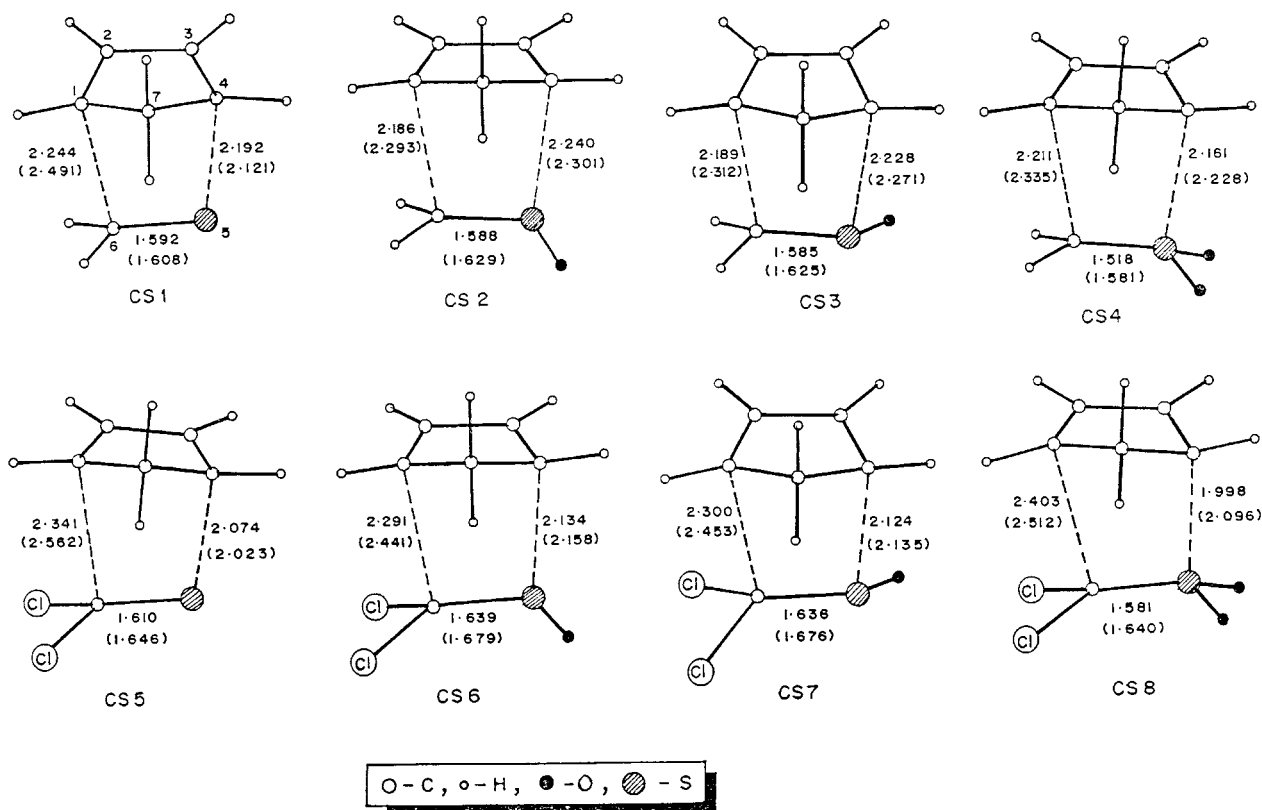


FIGURE 2. AM1 (PM3) optimized TSs for the reactions of cyclopentadiene with thioformaldehyde (1), thioformaldehyde S-oxide (2), thioformaldehyde S,S-dioxide (3), thiophosgene (4), thiophosgene S-oxide (5), and thiophosgene S,S-dioxide (6).

age of bond formation at the TS in the reactions of thiocarbonyl, sulfine, and sulfene show that the $C_4 \cdots S_5$ bond strength increase in the following order: thiocarbonyl < sulfine < sulfene. This can be understood by the following points: (i) the positive charge on the sulfur atom (see Fig. 1) increases from thiocarbonyls to sulfenes and (ii) the repulsion due to lone pair on sulfur on approaching diene is minimized on going from thiocarbonyls to sulfenes. That is, the progressive substitution of the oxygen atom on sulfur replaces lone pairs on sulfur. These two factors favor a strong $C_4 \cdots S_5$ bond formation at the TS as predicted by the calculation. The C_5-S_6 π bond is found to cleave 40 to 50% at the TS as can be seen from BC_i values listed in Table III and the chlorine substitution on the dienophile seem to weaken this bond at the TS to a higher degree. This is also clearly reflected in the broken C_5-S_6 bond listed in Figures 2 and 3.

The glide angles θ_1 and θ_2 collected from CS1–CS8 and AS1–AS6 TSs and presented in Table

I show that their values fall in the range 90–107° and are quite normal. The angle θ_1 is found to increase with crowding of oxygen atoms around sulfur atom. The difference in θ_1 and θ_2 values in these structures indicate the twisting or distortion of the diene in the TS, and happens due to the differing rates of formation of the new bonds. Slightly lower θ_1 , θ_2 , and ϕ values in the TSs AS1–AS6 over those in CS1–CS8 is due to the relative rigidity of anthracene over cyclopentadiene. In the ideal case, the twist angle will be zero, and a nonzero value of ϕ indicates twisting of the newly forming bonds from the C_s plane. The difference in ϕ for the *exo* and *endo* TSs—CS2 vs. CS3 and CS6 vs. CS7—can be understood on the basis of the secondary orbital interaction of the oxygen atom with the $C\pi$ of diene; the ϕ value is expected to be higher in *exo* TS than in *endo*. The highest value of ϕ found in CS1 and CS5 for the thioformaldehyde (1) and thiophosgene (4) reactions can be due to the twisting of the C_s plane by the repulsion of the lone pair on sulfur on the

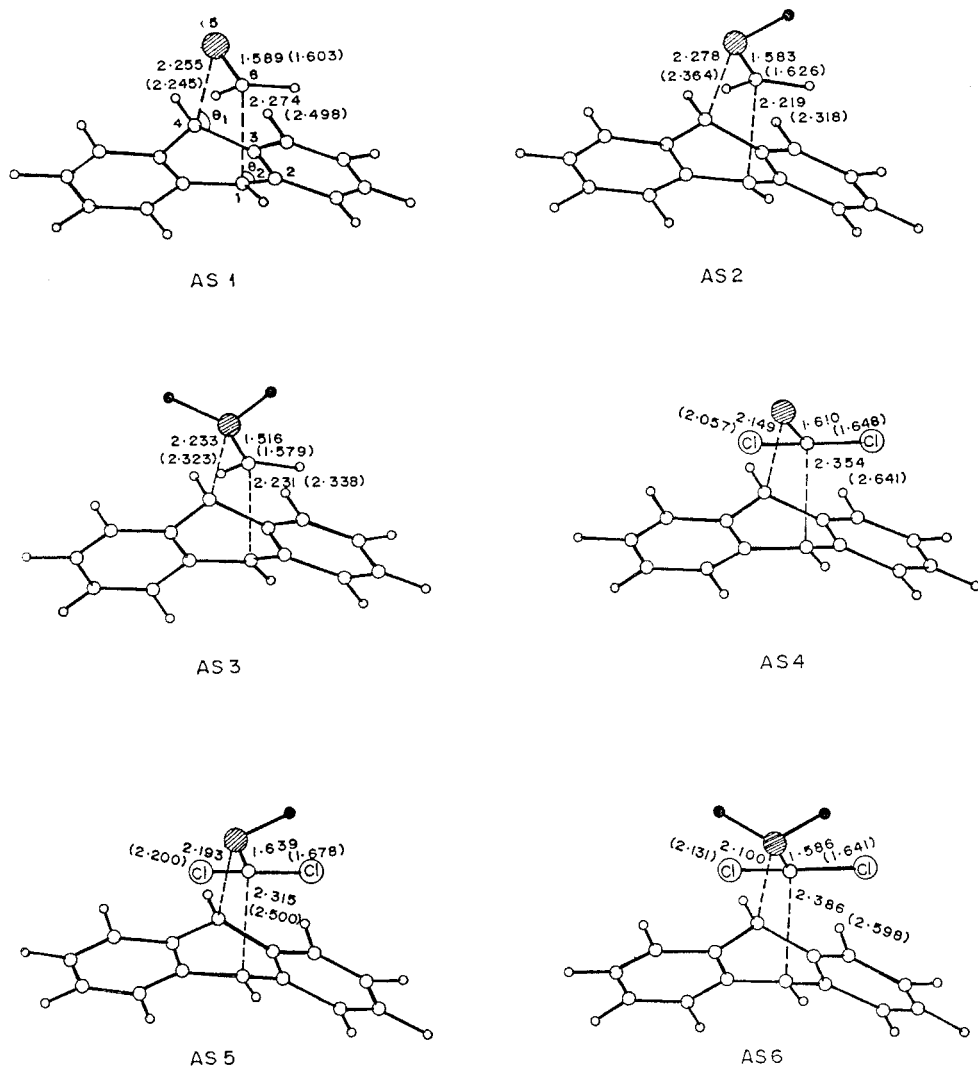


FIGURE 3. AM1 (PM3) TSs for the reactions of anthracene with thioformaldehyde (1), thioformaldehyde S-oxide (2), thioformaldehyde S,S-dioxide (3), thiophosgene (4), thiophosgene S-oxide (5), and thiophosgene S,S-dioxide (6).

approaching diene. During the reaction, both the thiocarbonyl carbon and sulfur atoms rehybridize from sp^2 to sp^3 , and this results in pyramidalization at these two sites and the extent of pyramidalization is found to be slightly more at the sulfur site than that at the carbon site.

Bond Order Analysis

Percentage of bond forming (BF_i) and cleaving (BC_i) at the TS (Table III) of various bonds as well as average percentage of bond make-break (BFC_{Ave}) are excellent parameters to explain the changes in degree of bonding during the reaction. AM1 BFC_{Ave} values fall around 50% and PM3

values are nearly 40%. BFC_{Ave} is indicative of the relative maturity of TSs in the reaction path for a series of reactions. BFC_{Ave} values for these TSs are found to be in the following order:

$$CS1 < CS2 \approx CS3 < CS4; \quad AS1 < AS2 < AS3; \\ CS5 < CS6 \approx CS7 < CS8; \quad AS4 < AS5 < AS6.$$

This reveals that the TS of sulfine reactions occur earlier than those of sulfene reactions, and the TS of thiocarbonyl reactions occur still earlier. This could have been responsible for the predicted order of reactivity. If two sets of the reactions involving dienophiles 1–3 and 4–6 are compared, the TSs of thiophosgene analogs occur slightly later than those of corresponding parent dienophiles. This

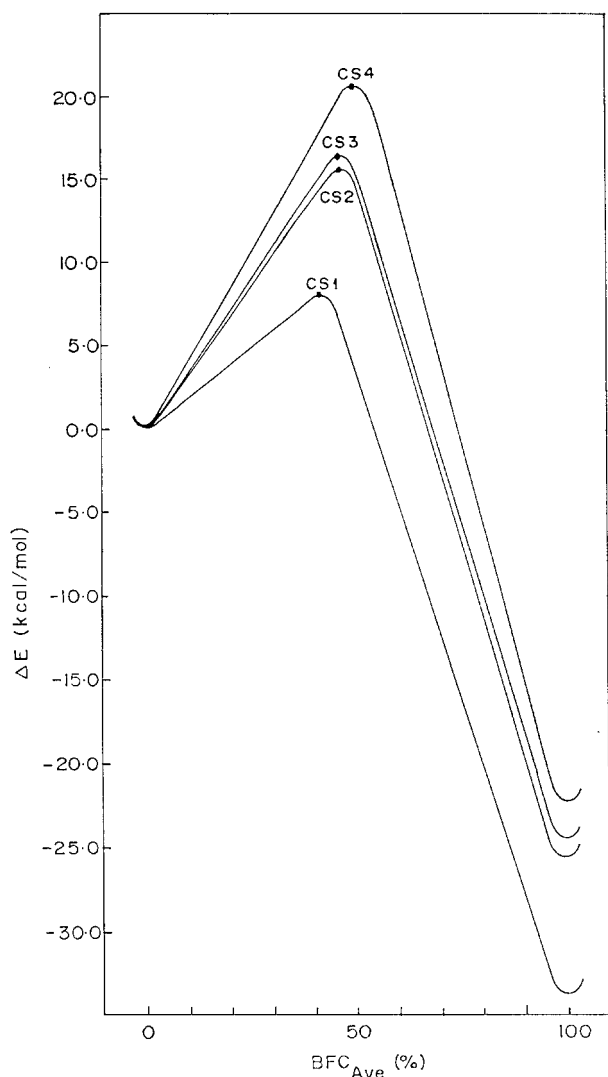


FIGURE 4. Plot of relative energy of TSs and products versus BFC_{Ave} ; 0% and 100% of BFC_{Ave} ; values denote reactants and products, respectively. Reactant state is taken as reference. The representative plot is drawn based on AM1 values and for the reactions of **1**, **2**, and **3** with cyclopentadiene.

suggests that the introduction of chlorine demands an increased deformation for both diene and dienophile for forming the TS, and this could have pushed the barrier. Steric crowding of oxygen atoms around sulfur in sulfines and sulfenes increase the deformation. In reactions involving cyclopentadiene as diene, the bond cleaving processes seem to dominate over bond forming processes whereas the trend is reversed in the reactions involving anthracene as diene. This can be seen from BC_{Ave} and BF_{Ave} listed for CS1–CS8 and

AS1–AS6 TSs in Table III. The change in the trend in anthracene reactions may be due to the increased BF_i value for the bond C_2-C_3 (Table III) in them, and this happens because formation of this C_2-C_3 double bond leads to aromatic stabilization of one of the benzene rings in dibenzothiabicyclic Diels–Alder adduct.

Energetics

Calculated activation energies reveal that Diels–Alder reactions involving thiocarbonyls, sulfines, and sulfenes with cyclopentadiene and anthracene are most favorable and they are fast. This can be seen by comparing the activation energy of the above reactions with that of typical reactions listed in Table II. A very low activation barrier obtained for the reactions of thioformaldehyde with cyclopentadiene and anthracene indicate that this reaction should be much faster, and it is worthwhile to note here a similar observation made based on MP2/6-31G* barriers [11] obtained for butadiene–ethylene and butadiene–thioformaldehyde reactions. For a reaction of chlorophenylsulfine with 2,3-dimethyl 1,3-butadiene, Zwanenburg and co-workers [3] have reported the experimental ΔH^\ddagger value 18.4 kcal/mol, and this can be compared to AM1 (PM3) barrier computed for the reactions of sulfines with cyclopentadiene that fall in the range 15–19 (25–27) kcal/mol (Table II). The above observations indicate that, of the two models employed, AM1 seems to give a reliable barrier while those of PM3 are higher by a few kilocalories.

The LUMO energies (Fig. 1) and q_{CT} values (Table II) seem to predict the following reactivity order: thiocarbonyl > sulfine > sulfene. That is, down the series LUMO values are progressively destabilized and the quantum of charge transfer from diene highest occupied molecular orbital (HOMO) to dienophile LUMO gradually decreased. In full conformity with the above trend the activation barriers (Table II) also show the same pattern, the barrier increased from thiocarbonyl to sulfene. Such a difference in reactivity between sulfine and sulfene has been reported by Block and others [7a]. This can be clearly seen from the position of the AM1 barriers of reactions of certain thiocarbonyls (**1**, **2**, and **3**) with cyclopentadiene. Figure 4 shows that the barrier is gradually increased and shifted to the right when going from thioformaldehyde to thioformaldehyde S,S -dioxide. One can also see the relative exothermic-

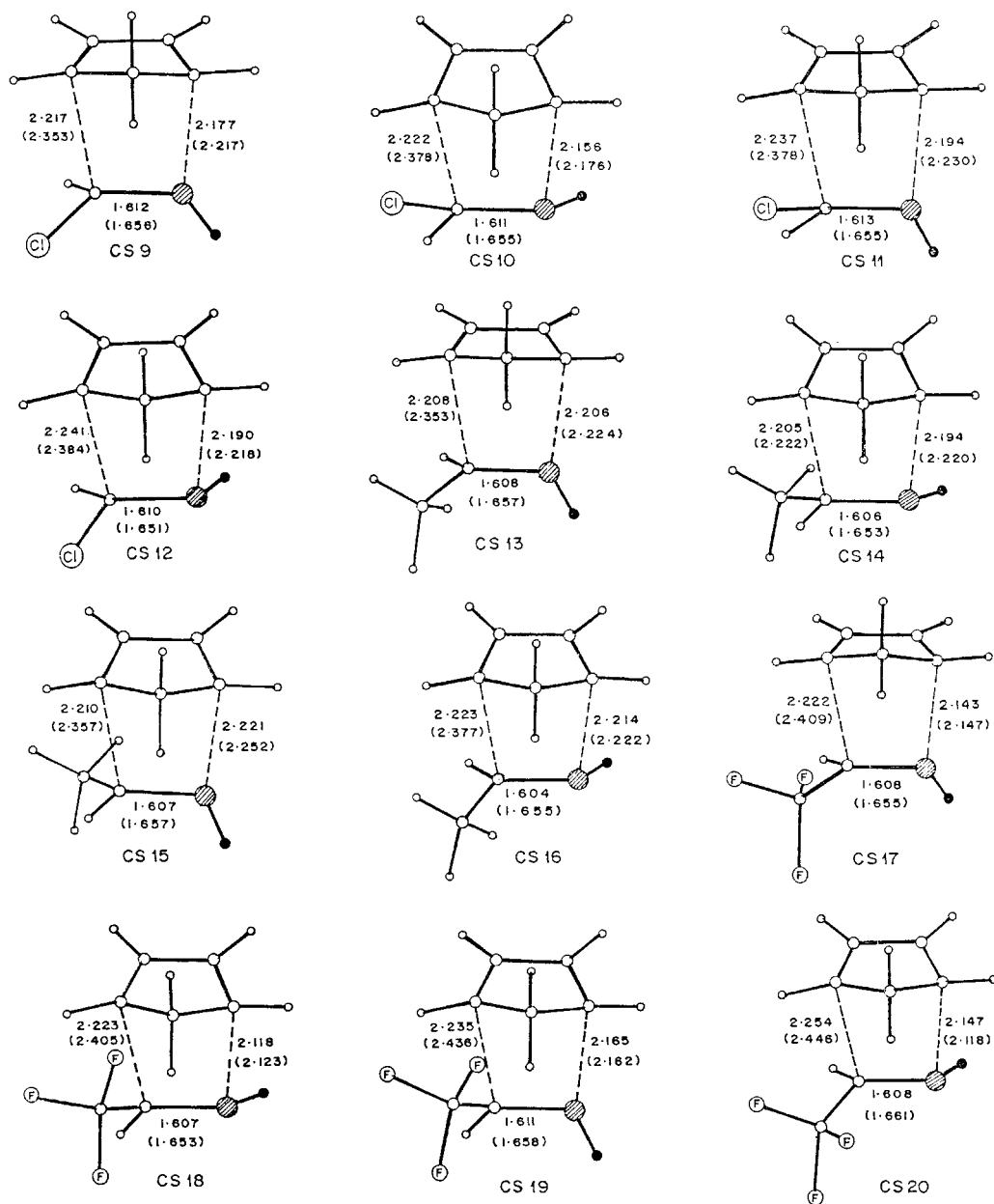


FIGURE 5. AM1 (PM3) TS geometries for the reactions involving monosubstituted Z/E sulfines with cyclopentadiene.

ity of these reactions from the figure. Further, the deformation analysis of activation barrier gives a clue for why the barrier should increase while going from thiocarbonyl to sulfene.

Deformation energy of diene DE1 and dienophile DE2 listed in Table II for the reactions of 1–6 reveal that both diene and dienophile deform to different extents in their reactions. More specifically, the extent of deformation of both reactants, indicated by the deformation energy, in-

creases from thiocarbonyl to sulfene. From thiocarbonyl to sulfene, the sulfur site is progressively crowded by oxygen atoms and this has been shown, by bond order and charge density analysis, to increase the reactivity of sulfur atom during the reaction. But this is not the only factor that decides the reaction course. The same oxygen atoms have also been shown to be responsible for increased deformation of both reactants while forming the TS. This latter factor should outweigh the former

TABLE I
Selected AM1 (PM3) geometric parameters and degrees of asynchronicity for the TSs.

TS	θ_1^a (deg.)	θ_2^a (deg.)	ϕ^a (deg.)	α^b
CS1	90.4(94.7)	94.5(92.0)	8.6(6.4)	0.012(0.080)
CS2	99.6(100.2)	95.3(94.7)	-4.3(-3.4)	0.012(0.002)
CS3	98.8(100.3)	97.5(96.3)	0.8(0.0)	0.008(0.009)
CS4	102.9(102.9)	96.7(96.0)	-2.8(-1.6)	0.011(0.023)
CS5	93.6(99.3)	92.2(93.8)	6.3(3.6)	0.060(0.118)
CS6	102.2(103.1)	96.3(94.3)	-3.0(-2.3)	0.035(0.062)
CS7	101.6(103.5)	96.3(94.9)	-1.8(-1.5)	0.040(0.069)
CS8	107.7(106.0)	95.0(94.2)	-5.4(-2.3)	0.092(0.090)
AS1	94.7(97.7)	92.3(89.9)	0.0(0.0)	0.004(0.053)
AS2	97.0(97.3)	95.4(94.8)	-1.2(-2.4)	0.013(0.010)
AS3	98.8(99.4)	93.8(93.4)	0.0(0.0)	0.000(0.003)
AS4	97.8(102.5)	93.5(89.5)	0.0(0.0)	0.046(0.124)
AS5	99.6(101.3)	94.7(92.6)	1.9(0.0)	0.027(0.064)
AS6	102.5(104.1)	93.2(90.3)	0.0(0.0)	0.064(0.100)
CS9	99.7(101.4)	95.9(95.5)	-1.9(-0.9)	0.009(0.030)
CS10	101.5(101.9)	95.8(93.6)	-4.7(-4.6)	0.010(0.032)
CS11	99.0(101.3)	96.9(96.3)	1.5(1.0)	0.011(0.036)
CS12	101.2(102.6)	97.5(95.0)	-1.3(-2.5)	0.015(0.044)
CS13	99.6(101.4)	95.7(94.9)	-3.4(-2.7)	0.000(0.028)
CS14	100.5(101.8)	96.3(95.1)	-4.1(-3.7)	0.002(0.023)
CS15	98.5(100.8)	97.1(97.0)	1.0(2.2)	0.002(0.034)
CS16	100.0(102.1)	98.0(96.1)	0.0(-1.5)	0.003(0.000)
CS17	100.9(102.8)	95.1(92.9)	-3.8(-4.2)	0.018(0.058)
CS18	101.5(103.3)	97.0(94.2)	-1.7(-2.7)	0.016(0.060)
CS19	100.2(102.6)	95.8(95.7)	0.0(2.4)	0.024(0.072)
CS20	101.7(103.5)	98.5(95.8)	1.0(0.0)	0.024(0.062)

^a $\theta_1 = 3-4-5$; $\theta_2 = 2-1-6$; $\phi = 4-5-6-1$.^bDegree of asynchronicity as calculated from $|r_{4-5} - r_{6-1}| / (r_{4-5} + r_{6-1})$.

and hence can lead to a gradual increase in the activation barrier.

Calculated activation energies show that the reactions involving various thiophosgenes (**4**, **5**, and **6**) should be relatively slightly slower than that of parent dienophiles (**1**, **2**, and **3**). The LUMO energies of thiophosgene dienophiles (**4**–**6**) are found to be more stabilized and q_{CT} values increased compared to the corresponding thioformaldehyde compounds (**1**–**3**). This should therefore increase the reactivity of thiophosgenes than thioformaldehyde systems, and this is anticipated. Earlier reports [3] also convey that electron withdrawing substituents on thiocarbonyl systems should increase the dienophilicity, but there is no clear-cut experimental evidence for which of the two is more reactive. On the contrary, both AM1 and PM3 activation barriers predict less reactivity for the thiophosgene dienophiles compared to their

parent systems. Such a trend is possible only if the steric factor offsets the electronic influence and dominates in determining the barrier. Deformation energy analysis is supportive of the above fact.

The reaction of sulfines (**2** and **5**) with cyclopentadiene can proceed through *exo* and *endo* selective TSs and in that the *endo* adduct should be preferentially formed in view of the secondary orbital stabilization due to the oxygen atom that is in *endo* position and the absence of *endo*-lone-pair repulsion. PM3 activation energies here correctly predict the experimental observation [7a] compared to AM1 barriers. The reaction energies calculated for these reactions show that they are exothermic, and their exothermicity is comparable with the typical reaction. Relatively, the reactions of thiophosgene dienophiles are found to be more exothermic. The high exothermicity of the reactions of thioformaldehyde with cyclopentadiene

TABLE II

Calculated AM1 (PM3) frontier orbital energy gaps (eV), quantum of charge transfer, activation and reaction energies (kcal/mol) for the reactions involving various thiocarbonyls (1–6) with cyclopentadiene (I) and anthracene (II), and deformation energy (kcal/mol) of the diene (DE1) and dienophile (DE2) at the TS.

		Diene + R ₂ C=X (Type A)							
X, R		ΔE_1^a	ΔE_2^a	TS	q_{CT}^b	ΔE^c	ΔE_r	DE1	DE2
I									
CH ₂ , {22.5} ^c	H	10.5(10.5)	11.0(11.0)		0.001(0.011)	28.5(32.1)	-26.0(-26.4)	16.9(16.1)	9.9(8.9)
S,	H	8.2(7.8)	9.2(9.4)	CS1	0.144(0.158)	8.6(16.3)	-33.2(-35.1)	12.3(12.5)	4.5(2.3)
SO,	H	8.7(8.0)	10.5(10.3)						
exo	O			CS2	0.045(0.117)	15.4(25.2)	-24.1(-22.5)	15.5(13.6)	6.1(4.4)
endo	O			CS3	0.043(0.122)	16.3(25.0)	-25.5(-23.9)	15.9(13.8)	6.2(4.5)
SO ₂ ,	H	8.4(9.1)	11.5(10.5)	CS4	-0.003(0.081)	20.5(31.4)	-22.1(-20.8)	21.4(18.1)	13.0(10.0)
S,	Cl	7.4(7.2)	10.0(9.9)	CS5	0.227(0.219)	14.0(17.4)	-20.9(-27.5)	16.6(17.6)	8.9(4.6)
SO,	Cl	7.8(7.4)	10.2(9.6)						
exo	O			CS6	0.109(0.157)	19.3(27.2)	-16.6(-18.3)	19.3(16.7)	10.0(5.8)
endo	O			CS7	0.112(0.166)	19.8(26.4)	-17.6(-18.7)	19.5(17.0)	10.5(6.1)
SO ₂ ,	Cl	7.4(8.5)	10.6(9.4)	CS8	0.096(0.155)	19.6(29.4)	-17.4(-19.3)	26.3(21.7)	14.6(12.5)
II									
CH ₂ ,	H	9.6(9.5)	9.7(9.7)		-0.046(-0.024)	28.7(31.0)	-31.3(-31.6)	18.4(16.6)	10.4(8.7)
S,	H	7.3(6.8)	7.8(9.0)	AS1	0.126(0.144)	10.5(17.6)	-33.3(-37.9)	12.1(11.2)	4.3(2.1)
SO,	H	7.7(7.0)	9.2(9.0)	AS2	0.013(0.098)	18.0(26.2)	-24.8(-25.5)	16.1(13.9)	6.6(4.6)
SO ₂ ,	H	7.5(8.1)	10.1(9.2)	AS3	-0.017(0.057)	24.5(34.0)	-21.1(-22.3)	21.9(18.4)	13.7(10.4)
S,	Cl	6.4(6.2)	8.7(8.6)	AS4	0.206(0.191)	18.2(20.7)	-19.2(-29.1)	17.4(18.9)	10.0(4.9)
SO,	Cl	6.8(6.4)	8.8(8.3)	AS5	0.082(0.144)	23.8(30.4)	-14.7(-18.8)	19.8(17.4)	12.1(6.7)
SO ₂ ,	Cl	6.5(7.5)	9.2(8.2)	AS6	0.085(0.164)	27.8(34.5)	-13.3(-18.9)	27.1(23.3)	17.5(14.1)

^a $\Delta E_1 = E_{HOMO}$ (diene) - E_{LUMO} (dienophile); $\Delta E_2 = E_{LUMO}$ (diene) - E_{HOMO} (dienophile).

^bQuantum of charge transfer from diene to dienophile.

^cExperimental barrier, Ref. 30.

TABLE III

AM1 (PM3) Percentages of bond cleavage and formation at the TS for the Diels–Alder reactions of cyclopentadiene with various C=S heterodienophiles (1–6).

TS	Bond cleavage (BC _{<i>j</i>}) at the TS			Bond formation (BF _{<i>j</i>}) at the TS			BC _{Ave}	BF _{Ave}	BFC _{Ave}
	1–2	3–4	5–6	2–3	4–5	6–1			
CS1	41.2(26.6)	54.1(50.2)	46.1(39.4)	35.3(24.6)	42.9(41.2)	32.9(20.1)	47.1(38.7)	37.0(28.6)	42.1(33.7)
CS2	50.0(36.6)	53.9(43.7)	45.7(34.5)	42.1(30.5)	45.3(35.0)	37.1(26.3)	49.9(38.3)	41.5(30.6)	45.7(34.4)
CS3	48.4(34.0)	54.8(44.3)	46.0(34.5)	41.0(28.7)	45.6(36.0)	36.7(25.2)	49.7(37.6)	41.1(30.0)	45.4(33.8)
CS4	54.4(39.0)	63.6(52.2)	46.4(35.7)	47.3(33.6)	49.5(41.1)	34.0(24.0)	54.8(42.3)	43.6(32.9)	49.2(37.6)
CS5	45.3(34.7)	65.6(63.5)	54.0(50.2)	41.3(33.0)	55.4(55.1)	33.9(23.8)	55.0(49.5)	43.5(37.3)	49.3(43.4)
CS6	52.8(37.7)	64.1(54.8)	51.6(39.3)	47.4(34.2)	56.2(47.4)	36.2(24.2)	56.2(43.9)	46.6(35.3)	51.4(39.6)
CS7	50.6(35.7)	64.9(56.3)	51.5(39.9)	45.7(32.7)	56.4(49.0)	35.1(23.4)	55.7(44.0)	45.7(35.0)	50.7(39.5)
CS8	53.3(41.1)	73.7(64.5)	58.5(43.6)	49.9(38.0)	59.9(54.8)	26.6(21.4)	61.8(49.7)	45.5(38.1)	53.7(43.9)
AS1	43.9(39.0)	37.5(24.0)	43.3(34.5)	69.3(49.5)	36.6(31.1)	31.1(19.5)	41.6(32.5)	45.5(33.4)	43.5(33.0)
AS2	46.7(37.2)	42.2(29.8)	44.2(33.6)	69.6(51.2)	42.5(32.3)	35.0(25.3)	44.4(33.5)	49.0(36.3)	46.7(34.9)
AS3	57.8(47.3)	47.9(35.4)	43.8(34.3)	75.3(59.2)	45.4(36.5)	32.5(24.1)	49.8(39.0)	51.1(39.9)	50.5(39.5)
AS4	57.2(59.7)	41.5(29.9)	52.6(51.4)	73.4(57.5)	49.7(52.8)	34.6(24.0)	50.4(47.0)	52.6(44.8)	51.5(45.9)
AS5	57.2(49.7)	43.0(28.1)	50.8(39.5)	67.3(50.0)	53.3(45.7)	34.8(23.3)	50.3(39.1)	51.8(39.7)	51.8(39.4)
AS6	70.1(63.5)	45.5(32.7)	57.9(43.7)	62.6(52.5)	58.1(54.5)	20.6(20.6)	57.8(46.6)	47.1(42.5)	52.5(44.6)

and anthracene show that they are also feasible in thermodynamic sense, in accordance with Hammond's postulate [28]. Finally, calculations predict that, in these reactions cyclopentadiene reacts faster than anthracene, and this is in agreement with the experimental observations [3] by Zwanenburg et al. on the reactions of thiophosgene S-oxide with cyclopentadiene and anthracene.

REACTIONS OF RHC=SO WITH CYCLOPENTADIENE

Diels–Alder reactions of monosubstituted sulfines with cyclopentadiene have been largely used in synthesizing various sultenes [7a, b]. Each geometrical isomer (Z/E) of such sulfines (**7**, **8**, and **9**) reacting with cyclopentadiene can form two stereoselective TSs that can lead to two distinct stereoisomeric products. Therefore, altogether there are four different TSs and products possible. The first two TSs in each set CS9 and CS10, CS13 and CS14, and CS17 and CS18 presented in Figure 5 are formed due to the reaction of the Z isomer while the latter two TSs in corresponding sets CS11 and CS12, CS15 and CS16, and CS19 and CS20 are due to the E isomer. Block and others [7a] have reported that cyclopentadiene reacted with Z-alkanethial S-oxide to give a single product *endo*-3-

alkyl-2-thiabicyclo[2.2.1]hept-5-ene-*endo*-2-oxide. There are no experimental reports on the reaction of the E isomer with cyclopentadiene. In the reactions of chlorophenylsulfine with 2,3-dimethyl 1,3-butadiene[3], it has been noted that the stereochemical relationship in the sulfine is predominantly retained in the product both from the Z and E isomers. The experimental activation enthalpy has been found to be 18.4 kcal/mol for both isomeric reactions. We have already mentioned that AM1 barrier compares reasonably well with experimental values while PM3 values are higher by 7–8 cal/mol and have shown that the methods employed here for studying the present set of reactions are therefore suitable. But it should be acknowledged that difficulties may arise if closely lying TSs are analyzed for stereoselectivity.

The FOE gaps, q_{CT} values presented in Table IV, indicate that the reactions of **7**, **8**, and **9** with cyclopentadiene (type B) are normal electron demand reactions as simple sulfine reactions are. The TSs computed for these reactions almost resemble the TSs formed during the reactions of other sulfines discussed earlier. Computed LUMO energies (Fig. 1), q_{CT} values, and activation barriers (Table IV) show that the reactivity of these sulfines increased in the following order: trifluoromethylsulfine > chlorosulfine > methylsulfine, and this

TABLE IV
Calculated AM1 (PM3) frontier orbital energy gaps (eV), quantum of charge transfer, activation and reaction energies (kcal / mol) for the reactions involving monosubstituted sulfines (**7–9**) with cyclopentadiene.

R	Cyclopentadiene + RHC=SO (Type B)				
	TS	q_{CT}	ΔE^\ddagger	ΔE_r	
Cl ^a	<i>exo</i> O, <i>exo</i> Cl	CS9	0.061(0.126)	17.6(25.9)	–21.2(–20.3)
	<i>endo</i> O, <i>endo</i> Cl	CS10	0.059(0.130)	18.3(26.0)	–18.4(–19.1)
	<i>exo</i> O, <i>endo</i> Cl	CS11	0.085(0.152)	17.5(26.3)	–22.6(–21.9)
	<i>endo</i> O, <i>exo</i> Cl	CS12	0.083(0.143)	18.1(25.3)	–21.7(–22.2)
Me ^b	<i>exo</i> O, <i>exo</i> Me	CS13	0.033(0.103)	18.6(27.4)	–20.1(–19.2)
	<i>endo</i> O, <i>endo</i> Me	CS14	0.031(0.109)	19.6(27.3)	–18.2(–18.2)
	<i>exo</i> O, <i>endo</i> Me	CS15	0.046(0.124)	19.1(28.2)	–20.7(–19.9)
	<i>endo</i> O, <i>exo</i> Me	CS16	0.044(0.117)	20.1(27.4)	–19.8(–20.0)
CF ₃ ^c	<i>exo</i> O, <i>exo</i> CF ₃	CS17	0.892(0.751)	15.9(24.0)	–19.7(–19.7)
	<i>endo</i> O, <i>endo</i> CF ₃	CS18	0.898(0.765)	17.5(23.5)	–16.8(–18.2)
	<i>exo</i> O, <i>endo</i> CF ₃	CS19	0.920(0.789)	16.8(24.0)	–20.1(–21.1)
	<i>endo</i> O, <i>exo</i> CF ₃	CS20	0.899(0.766)	17.5(24.7)	–19.9(–20.5)

^a ΔE_1 (Z/E): 8.2(7.7) / 8.2(7.6), ΔE_2 (Z/E): 10.2(9.7) / 10.3(9.8).

^b ΔE_1 (Z/E): 8.6(8.0) / 8.6(8.0), ΔE_2 (Z/E): 10.1(9.9) / 10.1(9.9).

^c ΔE_1 (Z/E): 7.7(7.1) / 7.7(7.0), ΔE_2 (Z/E): 11.4(11.2) / 11.4(10.5).

as mentioned above is a natural consequence of the increased dienophilicity with more electron withdrawing substituents. In trifluoromethylsulfine, the CF₃ group stabilizes the LUMO by negative hyperconjugation and thus renders it the most reactive. The reaction energy in the case of trifluoromethylsulfine are found to be the highest and that of methylsulfine the lowest in the series. When a monosubstituted sulfine has been reacted with cyclopentadiene four distinct but closely lying TSs have been obtained as anticipated. In that, with the Z isomer, the reaction leading to *exo* O *exo* R product is expected to have higher reaction energy (more exothermic) while the reaction leading to *endo* O *endo* R product is expected to have lower reaction energy (less exothermic) [29]. The trend in reaction energy is well predicted by AM1 and PM3 methods.

The Z isomer can form two stereoselective TSs—one *exo* O *exo* R (CS9, CS13, CS17) and another *endo* O *endo* R (CS10, CS14, CS18), and between them the latter should be lower in energy than the former. This can be explained by two factors: (i) secondary orbital stabilizations by the oxygen atom on sulfur and the substituent on the thiocarbonyl carbon atom and (ii) repulsion by the lone pair on sulfur with C π orbital of diene. In the former TS, the first factor is absent and second is present, resulting in net destabilization of the TS by at least a few tenths of a kilocalorie. This relative stabilization of *endo* O *endo* R over *exo* O *exo* R TSs has been observed to be responsible for the formation of *endo* selective product and has been termed by Houk and others as *exo*-lone-pair effect [11]. The same factors should guide the course of the reactions of the E isomer that can form again two stereoselective TSs—one *exo* O *endo* R (CS11, CS15, CS19) and another *endo* O *exo* R (CS12, CS16, CS20). On similar grounds one can anticipate that *endo* O *exo* R product should be selectively formed over the other. But the AM1 reaction barriers for these sulfine reactions (Table IV) show a reverse trend and PM3 barriers show an oscillating trend. Such a mixed trend in activation barrier from AM1 and PM3 models are not unanticipated especially when TSs are closely lying. A recent experimental report [7d] indicates that the energy of activation for (4 + 2) cycloaddition of an E-sulfine to 2,3-dimethyl 1,3-butadiene should be lower than that of its Z isomer. LUMO energies and q_{CT} values reveal that the E isomer involved in the reaction is more reactive than the Z isomer but the activation barriers show a mixed trend.

Conclusions

Diels–Alder cycloadditions of a set of sulfur-centered heterocumulenes, viz. thioformaldehyde S-oxide and thioformaldehyde S,S-dioxide and their thiophosgene analogs with cyclopentadiene as well as anthracene have been investigated through TS search by means of AM1 and PM3 methods and limited ab initio computations. Reactions of simple thioformaldehyde and thiophosgene with the same pair of dienes have been done for comparison. Computations reveal that these reactions pass through an asynchronous TS to form thiabicyclic products. Frontier orbital analysis show that all these reactions are concerted normal electron demand processes with C—S π^* orbital involving in the reactions. Sulfur being more electrophilic, it is involved in the reaction at an early stage leading to a stronger forming C₄ \cdots S₅ bond than the C₆ \cdots C₁ bond in the TS. The activation energy of the reaction of thioformaldehyde is expectedly much lower and the barrier increases with progressive addition of oxygen atom to sulfur. This has been shown to be due to the destabilizing effect of the oxygen atom on the LUMO in sulfines and sulfenes and increase of deformation energy at the TSs. Chlorine substitution on these heterocumulenes does not seem to increase their dienophilicity as expected. Between cyclopentadiene and anthracene, the former is more reactive than the latter, and the reactions of cyclopentadiene are more exothermic than the latter as anticipated. Calculated barriers agree reasonably with the available experimental observations. Deformation energy and bond order analysis provide new insight into the factors that play a major role in the reaction. Reactions of three monosubstituted sulfines, namely chloro, methyl, trifluoromethylsulfines with cyclopentadiene, have been investigated to observe the stereoselective preferences of the reactions. It is found from the computed barriers that the reactivity of these sulfines increased with the increasing electron withdrawing nature of the substituent. The Z and E isomers of these sulfines are observed to form four closely lying stereoselective TSs that could lead to four distinct products. In that, the *endo* O *endo* R TS and *endo* O *exo* R TS is expected to be stabilized by *exo*-lone-pair effect and secondary orbital stabilization, and therefore the corresponding products should be preferentially formed. Among the four possible

products and TSs, the *endo* O *endo* R selective reaction should be the most exothermic and should have low barrier. Our calculations predict the relative exothermicity of these reactions clearly, but the AM1 and PM3 barriers show a mixed trend in stereoselectivity as the TSs are closely lying.

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