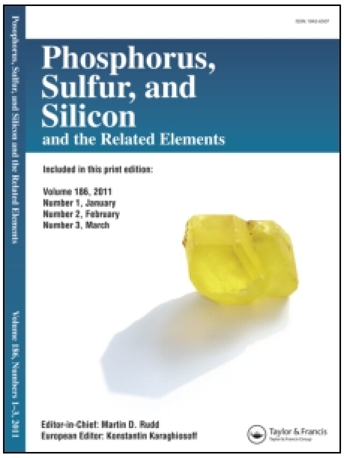

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Substituent Effect on the Electronic Structure of Sulfines: Molecular Orbital Treatment

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Substituent Effect on the Electronic Structure of Sulfines: Molecular Orbital Treatment

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The electronic structure and ground state properties of the gaseous sulfine H_2CSO *and some of its derivatives were studied at the RHF, MP2, and B3LYP levels. The calculations showed that the Z-isomer is more stable than the E-one and their difference in energy depends on their level of calculation, basis set, and substituent. The factors affecting the isomer stability are the electrostatic interactions, the steric factor, and* π*-electrons delocalization. The substituent has little effect on the geometry of the CSO moiety but greatly affects its charge distribution and polarizability. The* ΔE *value of the E- to Z-isomerization process via rotation of the S═O bond was calculated. The substituent has an appreciable effect on both the geometry and energy barrier of isomerization depending on its electronegativity, electrostatic attraction, and effect on* π*-delocalization over the molecule.*

Keywords Electrostatic interaction; MO calculations; substitution; sulfine; Z- to E-isomerization

INTRODUCTION

Sulfines (thiocarbonyl S-oxides) are four-centered heterocumulenes with a general formula, $R_1R_2C{=}S{=}O$. Sulfine and its related compounds occur naturally[1] in garlic and onion; the most famous sulfine is the propanethial S-oxide, which is the lachrymatory or tear-inducing factor of the onion and plays a key role in allium chemistry.[2,3] This group of compounds has great importance in biological and pharmaceutical activities, e.g. antibacterial and antifungal.[4]

Several reviews on the chemistry of sulfines cover most of the chemistry performed for such class of compounds.[3,5–7] Chemically, sulfines act as an intermediate in large organic reactions,[8,9] e.g., various 1,3-dipolar cycloaddition and Diels-Alder reactions, which are stereospecific

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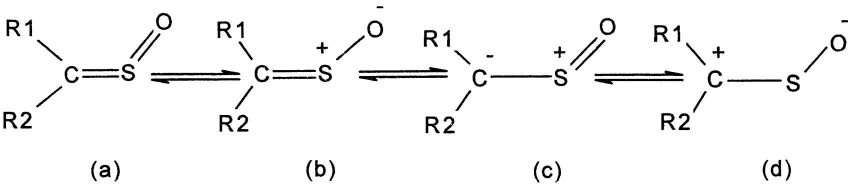
as the geometry of the sulfine is retained in the cycloadduct,[6] and also as ligands.[10–12] Other types of sulfine reactions are the thiophilic addition and carbophilic reactions which have been investigated in great detail.[2,6,13]

The simplest molecule of sulfines (parent) was a short-lived molecule and was prepared in the gas phase by flash vacuum pyrolysis of 1,3-dithiethane 1-oxide,[14] while the higher members of this class are stable and were prepared by various methods.[15–19] (Z) and (E) configurations of sulfines arise from geometrical isomerization about a carbon-sulfur double bond. The experimentally produced (E- and Z-) sulfine isomers which are produced in different ratios[17–22] are kinetically and thermodynamically controlled products,[20] respectively. The stereo of the product sulfine (E- or Z-configuration) depends on the method of preparation and the type of R_1 and R_2 groups attached to the carbon atom of sulfine group (R_1R_2CSO). The molecular structure of sulfines was experimentally identified by microwave analysis,[14] ^{1}HNMR spectroscopy,[23] photoelectron spectra,[24] and X-ray crystallography.[25,26]

Sulfine can be represented by the possible resonance contributory structures **a–d** (Scheme 1). Early structural analysis, however, revealed that the CSO fragment of sulfines is bent rather than straight. The equality of the C=S bond lengths in thioformaldehyde ($H_2C{=}S$)[27] and its S-oxide (sulfine) strongly suggest an unperturbed double-bond character of the sulfine C=S bond. However, the dipole moment of the sulfine, 2.994 D,[28] as well as the calculated charge distribution[29] point to polarized structure, suggest the importance of the resonance structure **b**.



SCHEME 1

The parent molecule was theoretically studied at different levels, e.g., structure,[30,31] its photo chemistry,[32] the UV/VIS spectral features,[33] vibrational frequencies,[34] gas phase thermochemical properties,[35–37] and the dimerization reaction.[38] Many experimental[23,28,39–41] works were performed to study the structure and factors affecting the stability of E- and Z-isomers and their interconversion, while there has been very little theoretical work.[1,31,35,42]

The main objectives of the present study are to

1. explore the geometric features of different substituted sulfines aiming to arrive at a reliable ground state electronic parameters using different levels of theory, Hartree-Fock (RHF), Electron Correlation (MP2), and Density Functional Theory (DFT) with reliable basis sets;
2. explore the effect of different substituents on the sulfine group, CSO, ground state properties, the relative stability of Z- and E-isomers, and charge density distribution;
3. investigate the structural factors that might underlie the biological and chemical reactivities of sulfines (cycloaddition, thiophilic, carbophilic, and tautomerism); and
4. compute the potential energy barrier (ΔE^*) of the E- to Z- interconversion and factors affecting its value.

METHOD OF CALCULATIONS

The very origin for the ambiguity in the formula representation of sulfine is the nonclassical nature of the conjugated bond systems arising from the substitution of the methine group at the mesoposition of the allyl anion by sulfur. If an octet expansion of the central sulfur (i.e., cumulenic formula **a**) is rejected, charge-separated Lewis-type structures such as (**b**) appear as a proper choice in the formula representation.

Ab initio studies of hypervalent sulfur-containing molecules are notoriously difficult and sometimes show large basis set effects.[43] Particularly, Burgers and colleagues found that standard G1 and G2 calculations with a 6–31G* basis set did not provide an accurate heat of formation of sulfine[1] and thus larger split-valence basis sets, 6-311+G(2df,2p), were required to obtain reliable equilibrium structures and spectroscopic data.[34] The closest geometry of the H_2CSO to the experimental one is that calculated at the B3LYP/6-311++G(3df,2p) level. On the other hand, the geometries calculated at the B3LYP, CASSCF, MP2, and CCSD levels[44] differ very little and it was found that there is not any significant multi-configurational component in the ground state of sulfine.

All molecules and conformers were optimized fully without any constraints. Three levels were used; (1) ab initio molecular orbital RHF,[45] (2) MP2,[46] and (3) the DFT (B3LYP);[47,48] thus the electron correlation was put into consideration with the basis sets 6-311++G**.[49] The polarization and diffuse functions were incorporated to deal with and describe the systems where electrons are relatively far from the nuclei. The nature of each stationary point was characterized by calculating the corresponding vibrational frequencies. The transition states are those with an imaginary frequency. The calculations were carried out using an GAMESS 6.4[50] package.

RESULTS AND DISCUSSION A-STRUCTURE

Methanthial S-Oxide

In this work, the geometrical structure of the parent sulfine was optimized at different levels of calculations: RHF, MP2, and B3LYP; the results are given in Tabel I, including the experimental results[1] and the other obtained theoretical results in literature[36] for comparison. The results show that the parent sulfine exists in a planar structure with bent CSO fragment and the value of CSO angle is nearly 114.7°. The comparison between these theoretical results with the experimental data reveals that the S—O and C—S bond lengths are more sensitive than the OSC angle to the level of theory or basis set. At the lower level of theory, the S—C and S—O bond lengths are overestimated with a maximum error of 0.217 Å and 6.5° for the CSO angle. By enlarging the basis set to 6-311++G** and inclusing the electron correlation, the experimental results are reproduced with a maximum error of 0.019A° and 0.6°. The best agreement with the experimental results is achieved when one puts the *f* function on heavy atoms; those of the MP2 level are close to the experimental results (Table I). The geometries calculated

TABLE I Bond Lengths (Å), Bond Angles (°), Atomic Charge and Dipole Moment (D) of Parent Sulfine Calculated at Various Levels

				Atomic charge			
Level of calculation	S—O	S—C	OSC	O	S	C	Dipole moment
HF/6-31+G(d,p)[a]	1.462	1.587	114.6				4.03
HF/6-311+G(d,p)[a]	1.456	1.585	114.6				4.09
HF/6-311+G(2df,2p)[a]	1.439	1.579	115.2				3.59
HF/6-311+G(3df,2p)[a]	1.433	1.576	115.5				3.50
B3LYP/6-31+G(d,p)[a]	1.498	1.625	115.1				3.12
B3LYP/6-311+G(2df,2p)[a]	1.479	1.611	114.9				3.19
B3LYP/6-311+G(3df,2p)[a]	1.472	1.607	115.2				3.11
B3LYP/6-311+G(d,p),S(3df)[a]	1.480	1.614	115.0				3.23
MP2/6-31+G(d,p)[a]	1.501	1.630	114.6				4.39
QCISD/6–31+G(d,p)[a]	1.510	1.626	113.2				4.41
HF/6-311++G(d,p)[b]	1.440	1.579	115.4	−0.69	0.72	−0.14	3.47
MP2/6-311++G(d,p)[b]	1.479	1.621	115.4	−0.51	0.60	−0.20	2.62
B3LYP/6-311++G(d,p)[b]	1.496	1.621	114.5	−0.44	0.51	−0.43	3.48
Experimental[c]	1.469	1.610	114.7				2.99

[a] Results taken from ref. [38] and references there in.
[b] Our results.
[c] Microwave spectrum results, Ref. [28].

at the B3LYP, CASSCF, MP2, and CCSD levels differ very little.[44] On the other hand, it was found that the multiconfigurational components in the ground state of sulfine do not affect the equilibrium geometry of the molecule.[38]

The C—S bond length in sulfine is calculated to be 1.621 Å at both the B3LYP and the MP2 levels with the basis set 6-311+G**, which is longer than that of H_2CS, 1.589 Å,[51] and is shorter than the C—S bond of thioformic acid (HCOSH), 1.806 Å.[52] These findings indicate a mainly perturbed double bond character of the C—S bond in sulfine. The elongation of the C—S bond in sulfine than in thioformaldehyde (H_2CS) represents its contamination by a single bond character. The same finding can be obtained for the other bond S—O, where its length lies between the pure single S—O, 1.658 Å[52] bond and that of pure S=O, 1.500 Å bond.

The characteristic charge separation is reflected in the calculated atomic charges, which is collected in Table I. The sulfur atom possesses a positive charge while both of the oxygen and carbon atoms of the sulfine group are negatively charged at all levels. The above results reveals the preference of the charge-separated resonance structures over the nature one.

Ethanethial S-Oxide

Gillies and colleagues[22] investigated the microwave study of (Z-) and (E-) ethanethial S-oxide, the internal structure, internal rotational barrier, and the electronic dipole moment. Microwave studies[24,53] and ^{1}HNMR spectroscopy[54,55] have identified the Z/E ratio of ethanethial S-oxide, as 97/3. Block et al.,[42] experimentally and theoretically, using RHF level of calculation, studied the conformational preference of CH_3CHSO molecule.

In this work, the two stereoisomers of methyl derivative are fully optimized at the three levels of work. The calculations show that the two isomers of ethanethial S-oxide have nearly the same geometrical parameters except for the $S_2C_3C_4$ angle, where it is greater by $\approx 5^\circ$ for the (Z-) isomer (Tables I and II). The methyl group has little effect on the geometry of the sulfine group where C—S and S—O bonds are only longer by 0.01 Å compared to the parent (Table I). When compared to the experimental results the MP2/6-311++G** level gives the best results and B3LYP one overestimates the results.

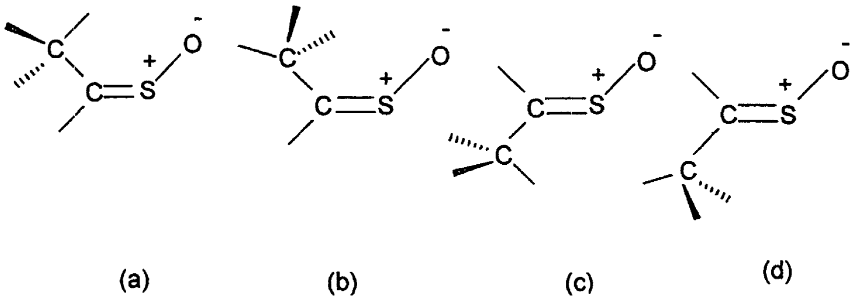
All levels of calculations show that the (Z-) form is less in energy than the corresponding (E-) isomer. The rotation around the C_3—S_2 bond or the free rotation of the CH_3 group around C_3—C_4 bond give the following conformers where (**a**) and (**b**) are (Z) forms (Scheme 2). Confomer (**a**) is

TABLE II Bond Lengths (Å) and Bond Angles (°) of Some Sulfine Derivatives Calculated at RHF,[a] MP2,[b] and B3LYP[c] Levels and 6-311++G Basis Set With the Bond Orders[d]**

	Z-isomer				E-isomer			
Compounds	S=O	C=S	CSO	SCX	S=O	C=S	CSO	SCX
CH_3CHSO	1.448[a]	1.587	114.9	126.8	1.447	1.587	114.9	121.3
	(1.484)[b]	(1.628)	(114.3)	(124.5)	(1.481)	(1.628)	(115.6)	(119.2)
	[1.488][c]	[1.632]	[113.6]	[126.0]	[1.502]	[1.632]	[114.1]	[121.4]
	1.600[d]	*1.520*			*1.620*	*1.530*		
FCHSO	1.444	1.592	115.2	125.7	1.450	1.595	112.0	119.7
	(1.481)	(1.637)	(115.2)	(125.0)	(1.484)	(1.642)	(112.1)	(118.7)
	[1.511]	[1.654]	[110.8]	[127.9]	[1.502]	[1.652]	[113.6]	[123.8]
	1.620	*1.510*			*1.590*	*1.500*		
CICHSO	1.438	1.589	115.6	126.1	1.442	1.590	113.0	120.3
	(1.479)	(1.639)	(114.6)	(124.2)	(1.481)	(1.642)	(112.9)	(119.0)
	[1.496]	[1.640]	[114.4]	[126.0]	[1.500]	[1.642]	[111.7]	[121.8]
FCH_3CSO	1.460	1.602	114.4	121.9	1.449	1.605	111.8	116.5
	(1.489)	(1.644)	(114.8)	(121.3)	(1.483)	1.646	(111.9)	(116.1)
	[1.508]	[1.650]	[110.8]	[120.7]	[1.501]	[1.648]	[113.7]	[115.9]
	1.60	*1.47*			*1.56*	*1.47*		
NH_2CHSO	1.482[a]	1.624	108.2	122.6	1.468	1.616	111.7	125.6
	(1.507)[b]	(1.645)	(107.7)	(119.1)	(1.490)	(1.644)	(113.4)	(123.6)
	[1.536][c]	[1.667]	[105.4]	[118.2]	[1.519]	[1.665]	[110.9]	[116.8]
	1.48[d]	*1.45*			*1.57*	*1.48*		
CHOCHSO	1.438	1.589	114.9	125.6	1.435	1.592	113.6	119.7
	(1.468)	(1.628)	(115.2)	(123.0)	(1.462)	(1.616)	(119.4)	(120.3)
	[1.495]	[1.639]	[114.1]	[126.4]	[1.491]	[1.632]	[118.6]	[123.5]
	1.64	*1.68*			*1.65*	*1.69*		
HCOOCHSO	1.430	1.589	117.9	131.9	[1.434]	1.590	113.6	121.8
	(1.468)	(1.618)	(117.0)	(116.9)	(1.486)	(1.630)	(113.3)	(115.8)
	[1.493]	[1.628]	[116.4]	[119.5]	[1.490]	[1.637]	[112.4]	[118.3]
	1.60	*1.66*			*1.57*	*1.65*		
C_2H_3CHSO	1.451	1.595	115.4	130.93	1.446	1.593	114.3	121.5
	(1.486)	(1.639)	(115.2)	(129.1)	(1.481)	(1.640)	(114.8)	(114.8)
	[1.506]	[1.645]	[113.8]	[129.7]	[1.501]	[1.645]	[112.3]	[125.9]
	1.58	*1.46*			*1.62*	*1.43*		

[a] Values calculated at the RHF level.
[b] Values calculated at the MP2 level.
[c] Values calculated at the B3LYP level.
[d] Values in italics refer to experimental results.

found to be more stable than the corresponding (**b**) form by 1.12 and 1.01 kcal/mol at the MP2 and B3LYP levels, respectively. On the other hand, the energy of (E-)forms (**c** and **d**) are 2.59 and 5.38 kcal/mol higher in energy than conformer (**a**), respectively, at the MP2 level and 2.36 and 5.08 kcal/mol at the B3LYP level. The RHF level shows that (**c**) and (**d**)



SCHEME 2

are 1.7 and 3.1 kcal/mol more in energy.[42] The difference in stability between the four forms is attributed to the electrostatic attraction (in the Z-form) between positive methyl hydrogen atom (in plane) and the negative terminal oxygen atom. The distance calculated between these two atoms is 2.56 and 2.57 Å at the MP2 and B3LYP levels, respectively. Another important reason for the stabilization of the (Z-)form is the orbital–orbital interactions. The π-type of orbital interaction is due to the formation of the aromatic 6-π electron system favoring form (**b**). The other orbital interaction type which stabilizes the (**a**) form is the formation of 6σ-MOs. This is reflected in the difference in the C_3—C4 bond length that is shorter in the (Z-)form.

The introduction of the electron donating methyl group to the sufine molecule increases and accumulates the charges on sulfur and oxygen atoms while the negative charge on the carbon atom decreases to −0.13 (Table III). This means that the SCO group becomes less polarized upon substitution.

Halogenated Sulfine

Table II shows the ground state properties of the optimized forms of (Z-) and (E-)fluoro- and chlorosulfines. The (Z-)form is calculated to be more stable than the (E-)form, the maximum difference is about 2 kcal/mol at the RHF level (Table IV), and the difference in energy increases with addition of electron correlation. The two isomers are coplanar and their bond lengths and bond angles depend on the type of the isomer. On the other hand, the existence of halogen atom does not appreciably alter the geometry of the sulfine group; the most affected bond is the C—S bond that elongates by about 0.01 Å. As shown in Table II, the S—O, C—S, and C—X bond lengths are longer in the (E-)form than the (Z-)form while the angles OSC and SCF are less by about 3° and 6°, respectively.

TABLE III Charge Density and Dipole Moment (D) of Some Sulfine Derivatives Calculated at RHF,[a] MP2,[b] and B3LYP[c] Levels and 6-311++G With the Experimental Data[d]**

	Z-isomer				E-isomer			
	Charges			Dipole moment	Charges			Dipole moment
Compound	O1	S2	C3		O1	S2	C3	
CH_3CHSO	−0.72	0.70	−0.15	3.88	−0.71	0.70	−0.11	4.31
	(−0.53)	(0.59)	(−0.19)	(2.87)	(−0.53)	(0.59)	(−0.15)	(3.25)
	[−0.46]	[0.43]	[−0.13]	[3.89]	[−0.46]	[0.45]	[−0.12]	[4.43]
				2.71[d]				
FCHSO	−0.69	0.66	0.29	3.96	−0.70	0.67	0.30	2.41
	(−0.52)	(0.54)	(0.18)	(3.13)	(−0.53)	(0.56)	(0.19)	(1.64)
	[−0.43]	[0.47]	[−0.18]	[3.93]	[−0.46]	[0.53]	[−0.23]	[2.30]
CICHSO	−0.68	0.71	−0.05	3.50	−0.69	0.73	−0.07	2.29
	(−0.50)	(0.57)	(−0.11)	(2.76)	(−0.51)	(0.59)	(−0.09)	(1.54)
	[−0.42]	[0.43]	[−0.46]	[3.55]	[−0.43]	[0.47]	[−0.49]	[2.60]
FCH_3CSO	−0.71	0.63	0.29	4.98	−0.88	0.81	0.22	3.07
	(−0.53)	(0.52)	(0.21)	(3.93)	(−0.55)	(0.55)	(0.20)	(2.11)
	[−0.45]	[0.45]	[−0.01]	[5.08]	[−0.47]	[0.48]	[−0.07]	[2.92]
NH_2CHSO	−0.79	0.55	0.09	5.46	−0.75	0.58	0.07	6.02
	−0.61	0.51	−0.05	3.94	−0.57	0.52	−0.05	4.56
	−0.62	0.51	−0.14	4.94	−0.58	0.51	−0.17	6.38
CHOCHSO	−0.67	0.79	−0.20	2.37	−0.66	0.83	−0.20	2.61
	−0.67	0.79	−0.20	2.37	−0.66	0.83	−0.20	2.61
	−0.49	0.68	−0.41	2.53				
HCOOCHSO	−0.64	0.79	−0.22	1.27	−0.66	0.81	−0.17	2.45
	−0.59	0.68	−0.16	2.29	−0.62	0.70	−0.11	2.74
	−0.47	0.73	−0.41	2.43				
C_2H_3CHSO	−0.71	0.71	−0.08	3.46	−0.70	0.72	−0.06	1.08
	−0.51	0.60	−0.15	2.55	−0.51	0.59	−0.12	2.88
	−0.53	0.61	−0.34	3.20	−0.51	0.63	−0.35	3.74

[a] Values calculated at the RHF level.
[b] Values calculated at the MP2 level.
[c] Values calculated at the B3LYP level.
[d] Values in italics refer to experimental results.

The total bond order of the parent sulfine bonds is greater than that of the halogenated sulfine, indicating less double bond character of CSO group bonds. The chloro derivative has a more double bond character than the fluoro one.

The Mulliken atomic charges on the different atoms of the halogenated (Z-)form is less than that of the (E-)form (Table III). The atomic charge on both oxygen and sulfur atoms in the two isomers is not appreciably affected by the fluoro substitution on the carbon, while the charge on the carbon atom changes to a less negative value in fluoro derivative owing to its high electronegatively. Thus, the fluorine substitution

TABLE V Total Energies[a] E_T (a.u), Conversion Barrier, ΔE^* (kcal/mol), Activation Energy[b] E_a (kcal/mol), Reaction Enthalpy[c] ΔH(kcal/mol), and Energy Difference, ΔE (kcal/mol) of Sulfine Compounds Calculated at the B3LYP/6-311++G Level**

Parameter	$E_T(Z)$	$E_T(TS)$	$E_T(E)$	ΔE^*	E_a	ΔE	ΔH
H_2CSO	−512.71885 (18.1)[20.28]	−512.71885 (16.57)[18.72]	−512.62999 (18.10)[20.28]	30.97	27.88	0.0	0.0
ClCHSO	−972.33786 (12.95)[15.66]	−972.27047 (11.98)[14.48]	−972.33395 (12.70)[15.52]	42.29	40.14	2.45	2.04
FCHSO	−611.97419 (13.76)[16.34]	−611.91554 (12.95)[15.27]	−611.97109 (13.50)[16.16]	36.80	35.44	1.96	1.52
CH_3CHSO	−552.05350 (35.91)[39.03]	−551.97214 (34.95)[37.74]	−552.04983 (35.84)[39.00]	51.05	48.80	2.30	2.20
NH_2CHSO	−568.11280 (29.30)[32.30]	−568.05616 (28.96)[31.58]	−568.09736 (29.04)[32.17]	35.54	34.48	9.69	9.30
CHOCHSO	−626.07381 (24.46)[27.77]	−625.99887 (23.52)[26.56]	−626.07337 (24.33)[27.68]	47.02	44.87	0.28	0.051

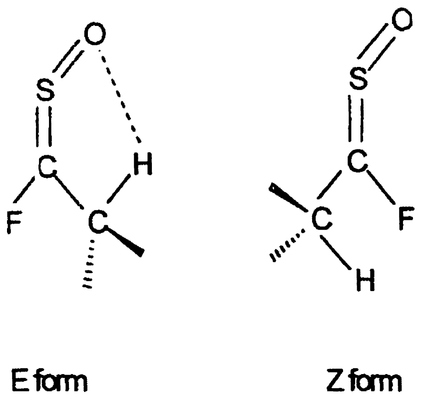
[a] Values in parentheses correspond to zero-point energy (kcal/mol) and thermal correction (TC) between two brackets (kcal/mol).

[b] $E_a = \Delta E^* + \Delta(ZPE) + \Delta(TC) + RT$.

[c] $\Delta H = \Delta E + \Delta(ZPE) + \Delta(TC)$.

decreases the polarization of C—S bond, the same results were obtained by both Bernardi and colleagues[56] and Lierop and Avoird[31] at the lower level of calculations. Thus, the fluoro sulfine molecule can exist only in either a native structure (**a**) or a charged structure (**b**) that is predominant. In case of the chloro derivative, the carbon charge is more negative at the three levels; the same trend is found for the charge on the sulfur atom, which becomes more positive, while the charge on oxygen atom becomes less negative (Table III). This means that the sulfinic group becomes more polarized in the case of the chloro sulfine and this facilitates the carbophilic reaction.

To examine the main affecting factors on the geometry and stability of both isomers, we examined methyl-fluorosulfine (Scheme 3). The results are shown in Tables II and VI. The results show that the two forms are coplanar and the (Z-) conformer is higher in energy than its E-one; the difference in their stability is 0.70, 0.68, and 2.15 kcal/ mol, at the three levels, respectively. Therefore, the electrostatic attraction and the orbital–orbital interaction are the factors stabilizing the (E-)form. The bond length of both S—C and S—O bonds are nearly the same for both isomers and also in mono-substituted molecules (Table II). On the other hand, the angle CSO alters to avoid the repulsion interaction between the negative halogen and oxygen atoms (increases in case of the (Z-)form).

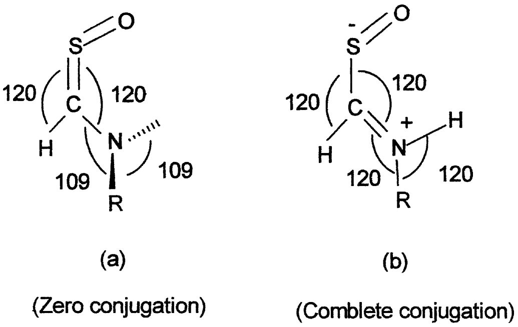


SCHEME 3 Electrostatic attraction.

Table III shows that the charges accumulated on the S—O bond are the same as those of a monosubstituent. The second result is the attraction of the negative charge on the carbon atom of the sulfine group to the electronegative fluorine atom, i.e., the main factor influencing the charge distribution on sulfine is the strength of substituent electronegativity.

THIOAMIDE S-OXIDE

The two conformers (Z-) and (E-) of thioamide S-oxide were optimized to the lowest energy stationary point and the results are given in Table II. The two conformers are planar (all atoms other than amino hydrogens) and the N atom is in its sp^2 hyperdization in case of the (Z-) form while it is pyramidalized in the (E-)isomer (Scheme 4). Table II shows that the S—O bond of the (Z-) form is longer by ≈0.01 Å



SCHEME 4

TABLE VI Bond Length (Å), Bond Angle (°), Twist Angle (°), Charge Density of Transition State (TS), Total Energies, E_T (a.u), Conversion Barrier, ΔE^* (kcal/mol), Energy Difference, and ΔE (kcal/mol) of Sulfine Compounds Calculated at the B3LYP/6-311+G** Level

Parameter	H_2CSO	ClCHSO	FCHSO	CH_3CHSO	NH_2CHSO	CHOCHSO
S=O	1.643	1.647	1.649	1.644	1.651	1.640
C=S	1.643	1.678	1.673	1.694	1.709	1.699
O—H		2.238	2.241	2.207	2.300	2.244
CSO	76.49	76.00	76.84	77.11	78.82	74.97
CSX	115.79	118.59	124.38	125.77	126.02	124.45
Twist angle	63.50	61.93	59.30	66.40	56.57	62.76
Charge						
O	−0.50	−0.51	−0.54	−0.53	−0.60	−0.46
S	0.43	0.49	0.44	0.41	0.34	0.46
C	−0.29	−0.27	−0.04	−0.24	−0.07	−0.25
E_T(Z)	−512.71885	−972.32936	−611.95904	−552.04616	−568.09932	−626.06326
E_T (E)		−972.32517	−611.95824	−552.04170	−568.08474	−626.06165
E_U (TS)	−512.62999	−972.25916	−611.90038	−551.96969	−568.04093	−625.98060
ΔE	0.0	2.62	0.50	2.79	9.14	1.01
ΔE^*	55.74	44.01	36.78	47.95	36.61	51.83

than the corresponding (E-)isomer, while the C—S bonds are of the same length. The difference in length between the two C—N bonds is 0.03 Å, where it is shorter for the (Z-)form. Therefore, the delocalization of the nitrogen lone pair of electrons into the π-system of the CSO group in the (Z-)form is more clear than in the case of the (E-) isomer leading to a partial double bond character of the C—N bond in both isomers, but its extent is higher in the (Z-) form. The rotation of the $-NH_2$ group around the C—N bond passes through a barrier of 9.95 kcal/mol at the MP2 level at angle 60° in which the system has maximum (O—H) distance (2.94 Å) and thus minimum electrostatic attraction. Comparing to the parent sulfine, $-NH_2$ group causes the greatest effect on the ground state properties of sulfine group. The C—S and S—O bonds elongate by 0.04 Å while the CSO angle decreases to 105.4° at the (Z-)isomer. On the other hand, the atomic charge distribution on CSO group remarkably, changes (Table III), leading to more electrostatic attraction between the terminal oxygen atom and H_5, consequently the cyclic forms arise in the case of the Z-form. The distance of $O\cdots H$ is calculated as 2.37, 2.22, and 2.17 Å at the RHF, MP2, and B3LYP levels, respectively. Thus, the (Z-)isomer is found to be less in energy by 8.28, 8.85, and 9.14 kcal/mol at the same levels. Another interesting result is the reduction of the polarizability of the C—S bond due to a decrease of negative charge on the carbon atom. Therefore, the main factors that contribute to the isomer stability are the electrostatic interaction, the σ-stabilization, and the electron delocalization.

CARBONYL SULFINES

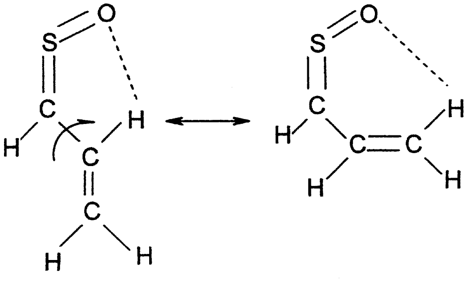
The calculations performed on both (Z-) and (E-) isomers of thioxoacetic S-oxide and thioxoethanal S-oxide showed that the two forms are planar and have nearly the same bond lengths, while only two bond angles differ where the CSO angle of the (Z-) form is greater by 4° than that of (E-)one and the SCC angle of (E-) form decreases by 10° (Table II). The carbonyl group substitution elongates only the C—S bond by 0.01 and 0.02 Å, respectively. The C_3—C_4 bond length of the two compounds (1.479 Å) indicates the existence of π-conjugation between the substituent and the CSO group. The most stable (Z-) conformer that contains the hydrogen atom is directed to the sulfinic oxygen atom, thus six- and five-membered cyclic forms are formed, respectively. The hydrogen bond formed in the two derivatives are 1.79 Å and 2.69 Å, respectively. Thus, the electrostatic interactions (repulsion or attraction) and the formed hydrogen bonds are the main factors determined by the relative stability of such conformers. In spite of such interactions, the (Z-)

structure of the acid derivative is higher in energy than its (E-)isomer, the difference in energy is calculated to be 2.23, 1.69, and 0.12 kcal/mol at the RHF, MP2, and B3LYP levels, respectively, while the (Z-)isomer of aldehyde is more stable by 2.57, 4.83, and 1.07 kcal/mol, respectively.

The charge distribution of the CSO group is appreciably changed upon carbonyl substitution. The carboxylic group increases the charges on the S—O bond in the two isomers, and therefore increases its polarizability while the charge on the carbon atom is not appreciably affected (Table III). This means that the electron-withdrawing effect of the S=O bond retards that of carboxylic group. On the other hand, the —COH group increases the S—C bond polarizability, the sulfur atom becomes more positive in both isomers, and the negative charge on the carbon atom increases only in the case of the (Z-)isomer, while the charge on the terminal oxygen atom is not affected by the substitution.

THIOACROLEIN S-OXIDE

The rotation of the vinyl moiety around the connecting C_3—C_4 bond results in two forms (cis and trans) in both the (E-) and (Z-)stereoisomers (Scheme 5). All levels of calculations showed the cis conformer to be a bit more stable (ΔE is only 2.0 kcal/mol), while the barrier to the internal rotation is calculated as 0.68 kcal/mol at MP2/6-311++G**. In both (Z-)forms (**a** and **b**), the distance O···H is 2.60 Å (case a) and 2.25 Å (case b). The π-conjugation is involved in both the (E-) and (Z-) isomers, the attractive electrostatic attraction between O···H is the effective factor for the over stability of the (Z-)isomer. The difference in energy between the two isomers is 5.56 kcal/mol using the B3LYP/6-311++G** level. The ground state properties of the most stable (Z-) and (E-) conformers are given in Table II. The (Z-)isomer is completely



(a) trans (b) cis

SCHEME 5

planar while the vinyl group in the (E-) form twisted around 40° out of the CSO plane, which is reflected on the elongation of the connecting C_3—C_4 bond in case of the (E-)form and at the same time decrease of its C=C bond length. This indicates a reduction in the π-conjugation of the (E-)form rather than the (Z-)form. This is nicely reflected in the rotational barrier value, which is 1.76 kcal/mol in the case of the (E-) isomer and 0.68 kcal/mol in the (Z-)one.

Table III depicts the net charge on each atom of both isomers of thioacrolein S-oxide, showing that in both isomers the pronounced effect of vinyl substitution is the withdrawing of the negative charge of the carbon atom of the sulfine group to the directly connected carbon atom, C_4 (Table III). In other words, the polarizability of such molecule is reduced.

B- (E-) To (Z-) INTERCONVERSION

The (E-) and (Z-)sulfine isomers are experimentally produced in different ratios depending on the type of the substituent, reaction conditions, and sterric hindrance. Watamabe and colleagues[20] found that the (E-)isomer of t-butyl phenyl sulfine, which is produced as a major, kinetically controlled product, is stable with regard to thermal isomerization, i.e., it does not change into the (Z-)form even after refluxing and while in the presence of a base it undergoes a facile isomerization, which means that the (Z-)isomer is thermodynamically more stable than the (E-)one.[2] The proposed mechanism reveals that the isomerization process depends on the rotation of the S=O group around the C—S bond which will easily undergo when the C—S bond possesses a more single bond character. Therefore, any substituent that increases the C—S bond polarization will help the isomerization process.

To our knowledge, the only theoretically studied[31] (E-) to (Z-) sulfine isomerization was done early using ab initio and INDO procedures for the parent sulfine. Two paths were studied: (1) the inversion path and (2) the rotation around the C—S bond. The results were poor with respect to the experimental values due to a small basis set used and the limited optimization.[57] The calculated barriers overestimated the experimental ones. The difference diminished upon adding a number of d-functions on the S atom.

In this part, the isomerization process through the rotation around the C—S bond is studied using the B3LYP level. The rotation of the C—O bond around the C—S bond was scanned at different angles and the results are given in Figures 1 and 2. TS structure was located for each molecule and confirmed by vibration frequency calculations. Different

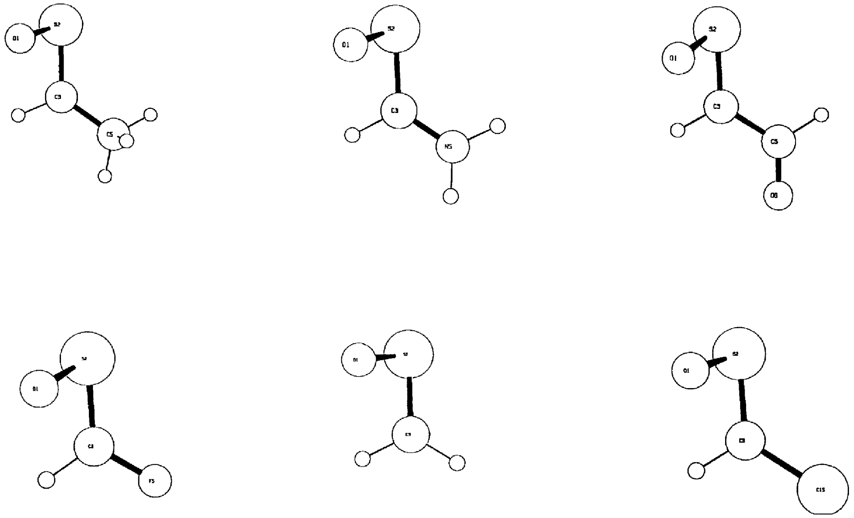


FIGURE 1 Structures of transition states of (Z-) to (E-)isomerization.

substituted sulfines are studied in a gas phase to elucidate the substituent effect on the isomerization process.

Table V shows the geometrical parameters of (E-) and (Z-) isomeric sulfines and their detected transition states. Comparing the bond lengths of the ground and transition states of H_2CSO molecule shows that both of the S—O and C—S bonds elongate in TS by 0.15 Å and 0.06 Å, respectively, at the B3LYP/6-311+G** level. The two hydrogen atoms do not lie in the same plane. The oxygen atom rotates by angle

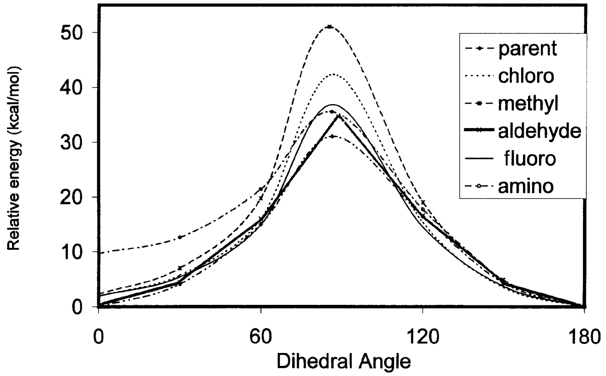


FIGURE 2 Variation of relative energy with the dihedral angle.

~63.5°, with respect to the nearest hydrogen atom and around 89.2° to the other one out of the molecule plane so the CSO angles decreases to 76.5° in TS. The elongation of these bonds indicates an increase in their single bond character in TS. The calculated atomic charges on different atoms in both states show that the polarization decreases in the case of the transition state. The calculated energy barrier using 6-311+G** basis set, $\Delta E^{*} = E_{s}\text{-}E_{TS}$ is 55.74 kcal/mol, which is still larger than the experimental value, 23.0 kcal/mol. The use of the 6-311++G** basis set decreases the value to 30.97 kcal/mol only while the corresponding activation energy is 27.88 kcal (Table IV).

The results for ethanethial S-oxide are depicted in Table V. The C—S and S—O bonds elongate upon rotation while the C=C bond becomes shorter by about 0.02 Å and the dihedral angle of oxygen atom is 66.4°. The electostatic attraction between the terminal oxygen atom and the methyl hydrogen atom decreases in spite of an increase of positive charge on the later one due to orientation of the oxygen atom toward sulfinic hydrogen with an O···H distance (2.207 Å) at the TS (Figure 1). The TS is higher than the (Z-) and (E-) states by 47.95 and 45.15 kcal/mol, respectively. This decrease in energy barrier relative to that of the parent is due to the stability of substituted TS due to electrostatic attraction with sulfinic hydrogen.

The isomerization of (Z-) to (E-)fluoro and chlorosulfines was studied, the bond lengths and angles of their TSs are closer to the E-form values and the distance O···H decreases to 2.241 Å, while the dihedral angle of oxygen atom is 59.3° in case of fluoro sulfine. The geometrical parameters of the CSO group are nearly the same for the two TSs. The energy barrier for (Z-) to (E-) isomerization is 36.78 kcal/mol for the fluoro compound and is higher by about 5 kcal/mol for the chloroderivative, which means that as the electronegativity of the substituent increases, the isomerization process becomes more easier.

The (Z-) to (E-)isomerization process of aldehydic sulfine passes through a barrier of 51.8 kcal/mol, which is high relative to that of the parent due to the high stability of the (Z-)form of aldehydic sulfine by a π-delocalization and electrostatic interaction. This is reflected in the elongation of the C_3—C_4 bond in TS relative to that of the (Z-) form while the CSO parameters are closer to those of the (E-)form.

The (E-) to (Z-)form of amino derivative isomerization passes through an activation barrier of only 27.47 kcal/mol. Table VI shows the geometrical parameters of TS, which has the largest CSO group bond lengths of the studied compounds. It also is interesting to note that the TS is geometrically closer to the Z-isomer; the O—H_5 distance is 2.30 Å, therefore, as in case of ethanethial S-oxide, this electrostatic attraction stabilizes the TS and thus decreases the energy barrier. The lesser value of the amino barrier in spite of the stability of the (Z-)form also is due to the longer bond length C—S (1.668 Å in (Z-) form to 1.709 Å in TS), which means it is a more single bond character and facilitates the rotation of the S—O bond.

CONCLUSIONS

The calculations show the best geometry for the parent molecule that calculated using electron correlation (MP2 and B3LYP) with a polarized basis set. The calculated atom charges on different centers at all levels indicate that the polarized structure is dominant.

The Z-isomer of the substituted sulfines is more stable than the E-one. The difference in their total energy depends on the level and basis set of the calculation and type of the substituent. This difference ranges from 0.33 in the case of thioxoethanal S-oxide to 8.06 kcal/mol in the case of thioamide S-oxide. The factors that increase the isomer stability are the electrostatic interaction, which were found in the case of R=Me, NH_2, HCO, COOH, and HC=CH_2, the sterric factor, and π-electrons delocalization, which occur in the case of R=NH_2 and —HC=CH_2 more than the other derivatives.

The substituent has little effect on the geometry of the CSO moiety in both isomers, where the C=S bond length increases only by 0.026 Å while the S=O bond varies by 0.032 Å than the parent case. The greates effect is found in the case of R=NH_2. On the other hand, the CSO angle increases in the case of the Z-case to avoid a sterric effect.

The oxygen atom possesses a negative charge in all molecules and the sulfur atom has a positive charge. The charge on the sulfine carbon atom depends on the nature of the attached substituent. The noticeable decrease in the C atom charge depends on the electronegativity of the attached substituent. Maximum change was found in the case of fluoride substituent, whereas the —COH and —COOH substitution did not appreciably affect the charge on carbon atom.

The calculated energy barrier ΔE value, at 6-311+G** basis set, of the (E-) to (Z-)isomerization process in case of the parent sulfine is still higher than the corresponding experimental. The difference is diminished when the basis set 6-311++G** is used. The substituent has an appreciable effect on both the geometry and energy barrier of isomerization. Both fluoro, amino, and chloro substitutions lower the barrier while the aldehyde substitution increases the barrier. The height of isomerization barrier depends on the electronegativity of the substituent, electrostatic attraction, stability of the E- or Z-forms, and

π-delocalization over the molecule. Geometrically, the bond length of both the C—S and S—O bonds elongate so the C—S bond acquires a more single bond character and thus facilitates the rotation of the S—O bond. The longest C—S bond is found in the case of —NH_2 substitution, which leads to the lowest barrier height.

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