جامعة أم القرى
كلية العلوم التطبيقيه
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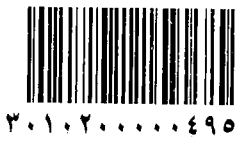

دراسة التركيب الالكتروني للأشكال المختلفة لبعض المركبات العضوية التي تحتوي على كبريت

رسالة مقدمه من

فاتن عبد المحسن الجفري

بكالوريوس في الكيمياء

وذالك كجزء من المتطلبات للحصول على درجة الماجستير في الكيمياء

المشرف

أ. د. عادل أحمد محمد

أستاذ مشارك بالكيمياء الفيزيائيه

جامعة أم القرى - كلية العلوم التطبيقيه

مكه المكرمه

1425

بسم الله الرحمن الرحيم

وزارة التعليم العالي
جامعة أم القرى
كلية العلوم التطبيقية

نموذج رقم (٨)

إجازة أطروحة علمية في صيغتها النهائية بعد إجراء التعديلات

الاسم (رباعي) : عبد الحسيب الحجازي ..... كلية : العلوم التطبيقية ..... قسم : الكيمياء .....
الأطروحة مقدمة لنيل درجة : الماجستير ..... في تخصص : الكيمياء .....
عنوان الأطروحة : ((دراسة التركيب الإلكتروني بطريقة الخلية لبعض المركبات العضوية التي تحتوي على الكبريت))

الحمد لله رب العالمين والصلاة والسلام على أشرف الأنبياء والمرسلين وعلى آله وصحبه أجمعين ..... وبعد :

بناءً على توصية اللجنة المكونة لمناقشة الأطروحة المذكورة أعلاه والتي تمت مناقشتها بتاريخ / / ١٤ هـ بقبولها بعد إجراء التعديلات المطلوبة، وحيث قد تم عمل اللازم ؛ فإن اللجنة توصي بإجازتها في صيغتها النهائية المرفقة للدرجة العلمية المذكورة أعلاه ...

والله الموفق ...

أعضاء اللجنة

المشرف	المناقش الداخلي	المناقش الخارجي
الاسم : د. عادل عمر	الاسم : د. [illegible]	الاسم : د. [illegible]
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يعتمد

رئيس قسم الكيمياء

الاسم : أ.د. عبد الله بن محمد العمري

التوقيع : .....

• يوضع هذا النموذج أمام الصفحة المقابلة لصفحة عنوان الأطروحة في كل نسخة من الرسالة .

الملخص العربي

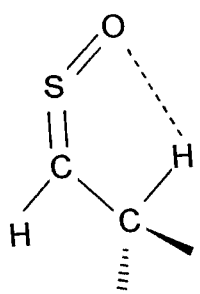
التركيب الالكتروني وخواص الحاله المستقره لمركب السلفين الاصلي (H_2CSO) في الحاله الغازيه وبعض المشتقات درست نظريا بالطرق التاليه: هارتري- فوك (RHF)، مولر- بلست (MP2) ونظرية كثافة الداله (DFT) وباستخدام قاعدة مجموعه مختلفه بدأ (6-31G) من الي (6-311+G**) لايجاد تأثير كلا من (electron correlation) وحجم واستقطابية قاعدة المجموعه على خواص الحاله المستقره لمركبات السلفين.

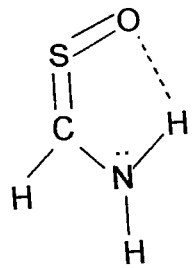
النتائج المتحصل عليها في دراستنا تم مقارنتها مع النتائج العمليه والنظريه المتاحه لنا. بالنسبه للجزيء الاصلي اظهرت النتائج ان افضل شكل فراغي تتوافق فيه القيمه النظريه للحاله المستقره مع النتائج العمليه تمت دراسته باستخدام (MP2 and B3LYP) مع قاعدة المجموعه (6-311+G**) . المركب الاصلي هو مركب مستوي مع انثناء لمجموعة السلفين (CSO). الشحنات المحسوبه على مراكز مختلفه عند كل المستويات تشير الي ان الشكل المستقطب هو $H_2C^--S^+=O$ او $H2C=S^+-O^-$.

العديد من المشتقات التي لها الصيغه العامه (R1R2CSO) درست عند نفس المستويات للمركب الاصلي لبحث تأثير الاستبدالات على درجة ثبات الاشكال المختلفه وخواص الحاله المستقره. والاستبدالات التي درست هي: (-F, -Cl, $-CH_3$, $-NH_2$, -COH, -COOH, $-CH=CH_2$, -Ph, o-, m- and p-methyl phenyl). وهذه الاستبدالات مختلفه في قيم السالبيه الكهربيه، في الحجم وفي القدره على تكوين رابطه هيدروجينيه.

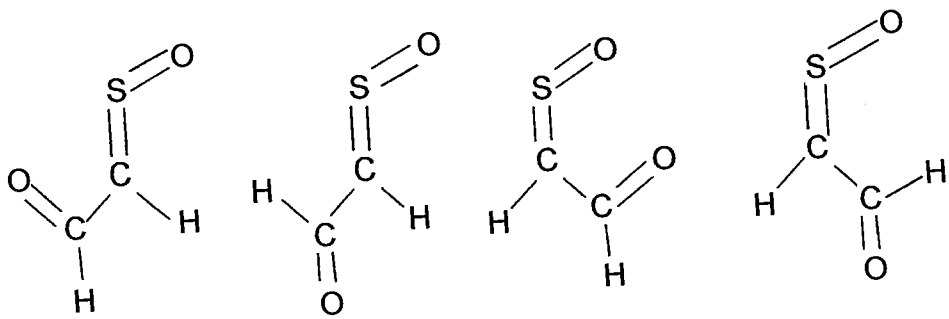
حسابات المدارات الجزيئيه تظهر ان الشكل (Z) اكثر ثباتا من الشكل (E). والفرق في طاقة الاستقرار يعتمد على مستوى الحسابات وعلى قاعدة المجموعة المستخدمه في الحسابات وكذلك يعتمد على نوع الاستبدال. هذا الفرق يتراوح في المدى من 0.33 في (thioxoethanal S oxide) الي 8.06 كيلو كالوري/مول في حالة (thioamide S-oxide) عند مستوى (MP2). العوامل التي تزيد من ثباتية (isomer) عن الاخر هي التجاذب او التنافر الالكتروستاتيكي مع

ذرة الاكسجين الطرفيه وعدم تمركز الكترونات باي. وهذه العوامل وجدت في حالة الاستبدالات التاليـه: (-Me, $-NH_2$, -COOH, -CHO, $-CH=CH_2$, Ph) حيث يتم التجاذب الالكتروستاتيكي بين ذرة الاكسجين واحدى ذرات الهيدروجين.

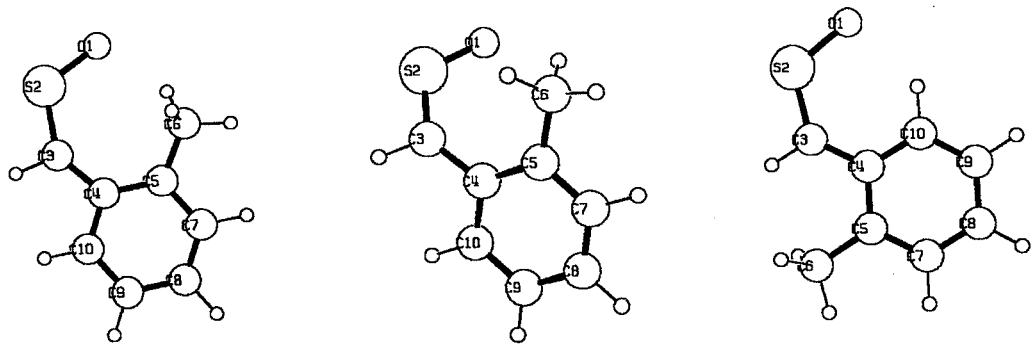




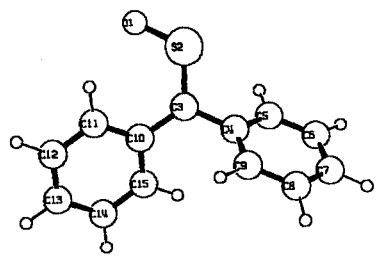
التنافر الالكتروستاتيكي يفضل الهيئه الفراغية من النوع (Z) في حالة الحمض والالدهيد. اطوال الروابط ورتبة الرابطة للرابطة (C-R) في حالة (R=-NH2, -CH=CH2 or Ph) تشير الي ان عدم التمركز للشحنه باي يكون اكثر وضوحا من المشتقات الاخرى.



العامل الفراغي ايضا يلعب دورا هاما في حالة الميثيل فينيل. مجموعة الميثيل في الموضع ميتا او بارا لا تؤثر على خواص مجموعة (CSO) بينما مجموعة الميثيل في الموضع اورثوا اظهرت نهايتين صغرى عند الزاويه الفراغيه 180° و 49° بينما عند الزاويه 90 تمثل حالة انتقاليه.



ومن ناحية أخرى في حالة (R1=R2=Ph) مجموعتي الفينيل تكون في وضع تناوب (rotate) بزاويه مقدارها (-52.75) و (-28.17) لتجنب التداخل الفراغي (sterric-interactions) و (nonbonding-interactions) بين ذرات الهيدروجين.



الاستبدالات لها تأثير قليل على خواص (CSO) في كل شكل ، بحيث ان طول الرابطة (C=S) يزداد بمقدار 0.026 انجستروم فقط بينما طول الرابطه (S=O) يتغير بمقدار 0.032 انجستروم مقارنة بالمركب الاصلي. والتأثير يكون بشكل واضح وكبير في حالة الامين. ومن ناحية اخرى الزاويه (CSO) تزداد في حالة الشكل (Z) نتيجة للتأثير الفراغي.

ذرة الاكسجين تمتلك شحنه سالبه جزيئيه في كل الجزيئات وذرة الكبريت تحمل شحنه موجبه جزيئيه. والشحنه على ذرة الكربون تعتمد على طبيعة الاستبدال المرتبط بها. والتغير الواضح في الشحنه على ذرة الكربون لوحظ عندما تكون المجموعه البديله ذات سالبيه كهربيه كما في حالة الفلوريد، حيث قلت الشحنه على ذرة الكربون من القيمه السالبه (-0.43) الي القيمه الموجبه او

القربيه من الصفر (-0.07). في حين ان كلا من الاستبدالات (-COH, -COOH) لا تؤثر على شحنة ذرة الكربون.

عملية التحويل (isomerization) من الشكل (Z) الي الشكل (E) تمت دراستها باستخدام (B3LYP/6-311G**). وهي تتضمن عمليه دوران الرابطه (S=O) خارج مستوى الجزيء. وقيمة (ΔE) المحسوبه نظريا في حالة السلفين الاصلي اعلى من المحسوبه عمليا بمقدار 27 كيلو كالوري/مول. الاستبدال له تأثير على كلا من (geometry) و (energy barrier) لعملية التحويل. كلا من الاستبدالات الفلور، الامين والكلور تقلل من حاجز الطاقه بينما الالدهيد يزيد من قيمة حاجز الطاقه.

طول الرابطه لكلا من الرابطتين (C-S) و (S-O) يزداد، لذلك الرابطه (C-S) لها خاصية الرابطه الاحاديه مما يسهل دوران الرابطه (S-O). استطالة الرابطه (C-S) يكون ملحوظ في حالة الامين حيث يؤدي الي اقل انخفاض في حاجز الطاقه. ارتفاع حاجز الطاقه في عملية التحويل يعتمد على السالبيه الكهربيه للاستبدالات، التجاذب الالكتروستاتيكي لثبات الاشكال (Z) او (E) وايضا تأثير الاستبدال في عدم تمركز الشحنه باي على الجزيء.

Umm Al-Qura University
Faculty of Applied Sciences
Chemistry Department

THE ELECTRONIC STRUCTURE OF DIFFERENT ISOMERS OF SOME ORGANIC COMPOUNDS CONTAINING SULFUR

By

Faten Abdul Mohsen Al-Jiffrey

B. Sc. In Chemistry

A Thesis

Submitted in Partial Fulfillment of the Requirements for the Master Degree in Chemistry

(M. Sc.)

Supervisor

Dr. Adel A. Mohamed

Associate Prof. of Physical Chemistry

Umm Al-Qura University

Faculty of Applied Sciences

Makkah Al-Mukarramah

1425 H

NOTE

The candidate Mrs. Faten Abdul Mohsen Al-Gafri has attended prerequisite courses for one academic year (1421 AH), in partial fulfillment for the degree of the master of the science, covering the following topics:

First Semester (1421 AH) : (12 hours/week)

1-Analytical Chemistry	91
2-Inorganic Chemistry	92
3-Organic Chemistry	90
4-Physical Chemistry	86

Second Semester (1421 AH) : (12 hours/week)

1-Analytical Spectroscopic methods	92
2-Analytical Separation methods	99
3-Electro Analytical Chemistry	95
4-Chemistry of Advance Spectroscopy	100
5-Special Topics of Inorganic Chemistry	100
6- Organic Stereo Chemistry	98
7-Theory and Mechanism of Organic Reactions	93
8-Surface and Catalysis Chemistry	97
9-Special Topics of Physical Chemistry	96
	Total (1229/1300)

She has successfully passed the examinations in these courses with an excellent grade (94.54%).

Head of the Chemistry Department	Supervisor of the post graduate studies
Prof. Dr. Abdul Hady Al-Aomri	Prof. Dr. Ali Abdul Hafez

قال تعالى:

((إنا لا نضيع أجر من أحسن عملا))

(سورة الكهف.30)

TO MY DEAR

FATHER AND MOTHER

TO MY SON

AL-SHAHEED

ACKNOWLEDGEMENT

ACKNOWLEDGEMENT

Thanks to Allah the Almighty for helping me during all stages of my life.

I would like to express my appreciation to the supervisor Dr : Adel A. Mohamed, The Associate Prof. of Physical Chemistry, Department of Chemistry, Umm Al-Qura University, Makkah Al-Mukarramah, for his kindness, true assistance, suggesting the subject and continuous advice with valuable criticism, supervision, guidance and encouragement during all stages of this research.

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Chemistry, Umm Al-Qura University and Mr. Abdul wahab Auoni for their continuous help, encouragement, care and facilities offered.

I wish to express my deepest thanks to all colleagues and students at the Department of Chemistry.

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SUMMRY

SUMMARY

The electronic structure and ground state properties of the gaseous parent sulfine H_2CSO and some of its derivatives were studied at the levels Hartree Fock (HF), Möller Plesset at the second level (MP2) and Density Functional Theory (B3LYP). Various basis sets were used starting from 6-31G up to 6-311+G** to find out the effect of both electron correlation and size of basis set and its polarization on the ground state properties of such group of compounds.

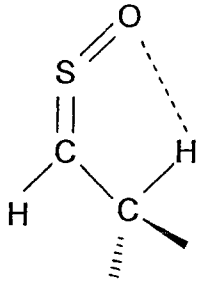
The results obtained were compared to those available in literature (experimental and theoretical). These findings shows that for the parent molecule the best geometry and thus the closest theoretical values of the ground state to the experimental ones are those calculated using electron correlation (MP2 and B3LYP) with a polarized basis set as 6-311+G**. That is due to the existence of octet central sulfur atom. The parent compound is planar with bent sulfine group (CSO). The calculated atom charges on different centers at all levels indicates that the polarized structure is the dominant one, $H_2C^-—S^+=O$ or $H_2C=S^+—O^-$.

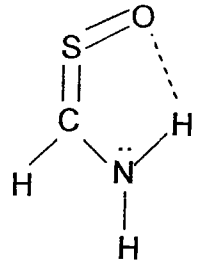
Many derivatives of the general formula, R1R2CSO were studied at the same levels of the parent to investigate the effect of such substituents on the stability of E- and Z-isomers and their ground state properties. The substituents studied are -F, -Cl, $-CH_3$, $-NH_2$, -COH, -COOH, $-CH=CH_2$, -Ph, o-, m- and p-methyl phenyl. These substituents

have different values of electronegativity, volume and ability for hydrogen bonding.... etc.

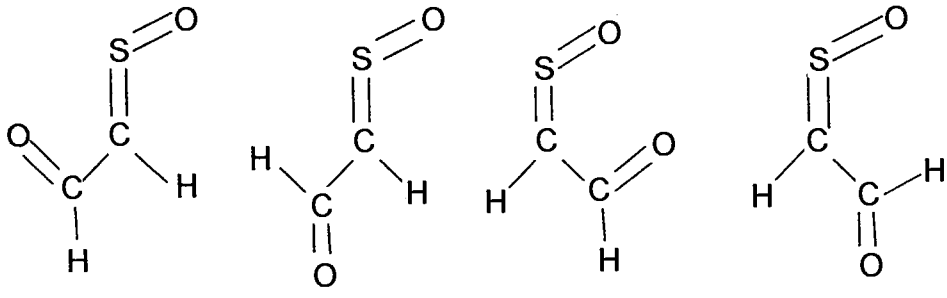
The MO calculations show that the Z-isomer is more stable than the corresponding E-one. The difference in stabilization energy depends on level of calculation and basis set of calculations and also on type of substituent. This difference ranges from 0.33 in the case of thioxoethanal S-oxide to 8.06 kcal/mol for thioamide S-oxide at MP2/6-31+G*. The factors that increase the isomer stability are electrostatic interaction attraction or repulsion, with the terminal oxygen atom and π-electrons delocalization.

These factors were found in case of R = Me, $-NH_2$, -COOH, $-HC=CH_2$, -HCO and Ph. In these cases the electrostatic attraction occurs between the oxygen atom and one hydrogen atom of R group.

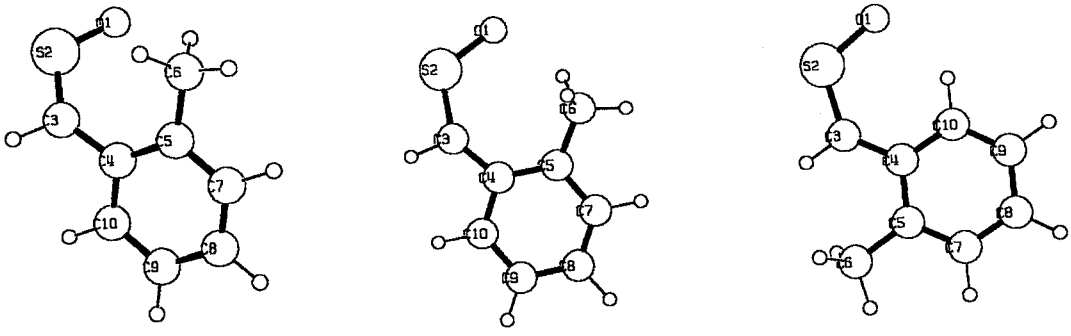




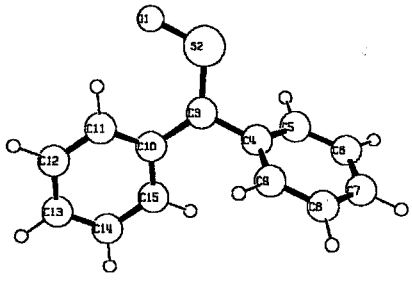
The electrostatic repulsion prefers the same Z-conformer in the case of acid and aldehyde. The bond length and bond order of C-R bond in when of R = NH_2, $-HC=CH_2$ or –Ph indicate the π-delocalization more than the other derivatives.



The steric factor also plays an important role in the case of methyl phenyl cases. The methyl group in m- or p-positions has no effect on CSO group while the o-methyl group results in existence of two minima (180° and 49°) while (θ = 90 ° and 0 °) are a transition states.



On the other hand, when R1 = R2 = Ph, the phenyl groups rotate by -52.75 ° and -28.17 ° angles to avoid the steric and nonbonding interactions.



The substituent has a little effect on the geometry CSO moiety in both isomers, where C=S bond length increases only by 0.026 A ° while the

S=O bond varies by 0.032 A ° than the parent case. The great effect is found in case of R = NH_2. On the other hand, the CSO angle increases in the case of Z-isomer by 7.2 ° to avoid steric effect.

The oxygen atom possesses a negative charge in all molecules and sulfur atom has a positive charge. The charge on sulfine carbon atom depends on the nature of the attached substituent group or atom. The noticeable change in the charge on C atom was found when the attached substituent is electronegative substituents where its charge decreases its negative value, maximum change was found in case of floride substituent where it changes from -0.43 at parent to -0.07 on substituent at B3LYP/6-311G**, whereas the –COH and -COOH substitution does not affect the charge on carbon atom.

The E- to Z-isomerization process was studied at B3LYP/6-311G** level. The isomerization was performed via rotation of S=O bond out of the sulfine plane. The calculated ΔE value in case of the parent sulfine is higher than the corresponding experimental value the difference is calculated to be 27 kcal/mol. The substituent has an appreciable effect on both geometry and energy barrier of isomerization. Both of flouro, amino and chlouro substitution lower the barrier while the aldehyde substitution increases the barrier.

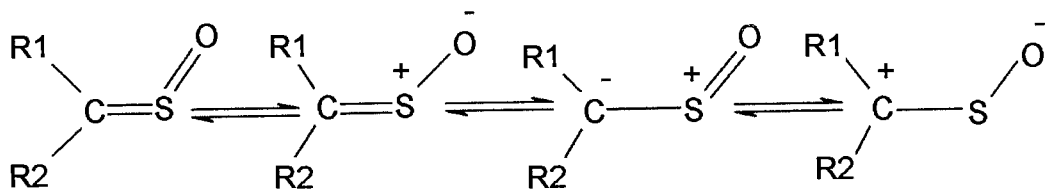
Geometrically, the bond length of both C-S and S-O bonds elongate, so the C-S bond acquire a more single bond character and thus

facilitate the rotation of S-O bond. The longest C-S bond is found in case of $-NH_2$ substitution, which leads to the lowest barrier height. The height of isomerization barrier depends on the electronegativity of the substituent, electrostatic attraction for that stability the E- or Z-forms and effect of substituent in π-delocalization over the molecule.

INTRODUCTION

INTRODUCTION

Sulfines are thiocarbonyl S-oxides and as such are usually represented by structure (**A**), other possible resonance contributory structures being **B-D**.



(A) **(B)** **(C)** **(D)**

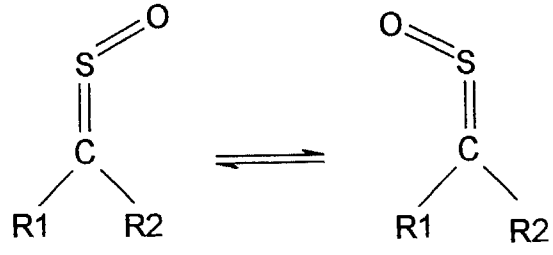
The parent compound (R1 = R2 = H)[1] and halogen substituted sulfines[2] are fairly unstable, while a number of alkyl- and aryl- substituted sulfines were isolated and characterized by spectroscopic tools and X-ray crystallography[3,4].

The molecular structure of the parent gaseous sulfine itself was identified by its microwave analysis[5] and photoelectron spectra[6]. Early structural analysis, however, revealed that the CSO fragment of sulfines is bent rather than straight. The CSO angle of 114.7 ° could be determined for the planar molecule. The bond lengths of the bonds C=S and S=O were found to be 1.61 A° and 1.47 A°, respectively. The equality of the C=S bond lengths in thioforamaldehyde ($H_2C=S$)[7] and its S-oxide (sulfine) strongly suggests unperturbed double-bond character of the sulfine C=S bond. However, the dipole moment, 2.994 D[8], of the

sulfine as well as the calculated charge distribution[9] point to polarized structure, this suggesting the importance of the resonance structure (**B**).

The very origin for the ambiguity in the formula representation of sulfine is the non classical nature of the conjugated bond systems arising from the substitution of the methine group at the meso-postion 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 formula representation.

The bent structure of the sulfine group implies that sulfines having unlike flaking substituents R1 and R2, may exist in two different geometric forms (E- and Z-).

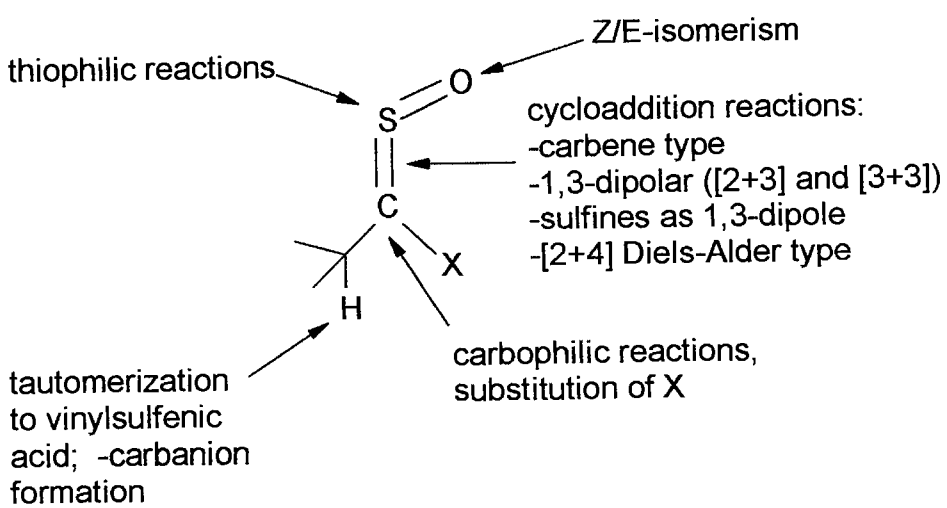


These two isomers are expected to be distinguishable as individuals or perhaps even physically separable, depending on the rate of interconversion. The experimentally produced (E- and Z-) sulfine isomers are kinetically and thermodynamically controlled products[10], respectively.

The most famous sulfine is propanethial S-oxide, which is the lachrymatory factor of onion[11]. Sulfine and related compounds occur naturally[1] in garlic and onion such as diallyl disulfide, dipropyl di-

sulfide, ... etc. In onion they produce propanethial S-oxide (sulfine)[12], which plays a key role in allium chemistry and which is responsible for the well-know lachrymatory effect of an onion[13]. This group of compounds has great importance in biological and pharmaceutical activities. The lachrymatory factor of the onion allium cepa has been identified as Z-ethyl sulfine[14]. Lachrymatory, or tear-inducing, quality of an onion is only one example.

Certain extracts of garlic and onions are antibacterial and antifungal[12]. Other extracts are antithrombotic, that is, they inhibit blood platelets from forming thombi (aggregations of themselves and the protein fibin). In short, they prevent clotting of blood. Also, they were used as an antiseptic in the prevention of gangrene in the two world wars[12].



Several reviews on the chemistry of sulfines have appeared over the years, covering most of the chemistry performed for such class of

compounds[13, 15-17]. Chemically, sulfines work as an intermediate in the large organic reactions like aminolysis reaction[18,19] and also they can act as ligands[14,20,21].

Sulfine compounds act as intermediaty in various Diels-Alder reactions aiming, for instance, to bicyclic sultenes[15]. Thus [4+2] cyclo-addition is stereospecific as the geometry of the sulfine is retained in the cycloadduct[16]. Another type of sulfine reactions is the thiophilic addition reactions which have been investigated in great detail[16,22].

The third type of sulfines chemical reactions are carbophilic reactions which can be accomplished when a good leaving group X is present, e.g. X for Cl displacement with sulfur nucleophiles has been accomplished[11]. Many experimental[8,23-26] and theoretical[1,27-29], using different low levels and various basis sets, studies were performed to investigate factors affecting the stability of E- and Z-isomers and their interconversion. The interconversion barriers and electronic properties of ground and excited states and spectra were also determined. The effect of substituents on the above properties was analyzed[27]. It was found that both steric and electronic effects are operating simultaneously to influence the stereochemistry of sulfines[30].

AIM OF THE WORK

The main objectives of the present study are to:

1-Explore the geometric feature of different substituted sulfines aiming to arrive to a reliable ground state electronic structural parameters using different levels of theory, Hartree-Fock (HF), MP2 (electron correlation) and Density Functional Theory (DFT), with various basis sets.

2-The effect of substituents of different power on sulfine group CSO, the stability of the Z- and E-isomerization process and charge density distribution.

3-Invistigate the structural factors that might underlie the biological and chemical reactivities of sulfines (cycloaddition, thiophilic, carbophilic and tautomirism).

4-Compute the potential energy barrier of the E→Z interconversion (isomerization) and the factors affecting its value, using high level of calculations (B3LYP) and big basis set (6-311G**).

CHAPTER ONE

LITERATURE

SURVEY

1.1. SPECTRAL STUDIES

1.1.1. IR SPECTRA

The parent sulfine (thioformaldehyde S-oxide) which is a short-lived gas phase species, H_2CSO, is the proto type for the sulfine. Gas phase IR spectra of H_2CSO and D_2CSO consist of strong absorption bands at 762 and 1175 cm^{-1} and a weaker band at 1355 cm^{-1}, a board feature also appear at 2985 cm^{-1}. Similar stop-flow experiments using DMSO-d_6 gave the strong C-type band at 602 cm^{-1}. The very strong band at 1189 cm^{-1} can be assigned as the CSO symmetric stretching[31].

E. Suzuki et al.[32] performed study of the matrix IR spectra for sulfine (À species) and sulfine-d_2 (À species). They found seven vibrations of À species and two vibrations of À species expected for sulfine. In the CH_2 stretching region, four very weak absorptions were observed: two sharp bands at 3117 and 3013 cm^{-1} and two broad bands at 3103 and 2987 cm^{-1}, the sharp bands were assigned to the CH_2 stretches of the monomer. In the CD_2 stretching region, three very weak bands were observed at 2339, 2276 and 2180 cm^{-1}. The bands at 2339 and 2180 cm^{-1} were assigned to CD_2 stretches. In the CH_2 scissoring region, three bands were observed at 1397, 1366 and 1357 cm^{-1}. The bands at 1397 and 1357 cm^{-1} have been assigned to CH_2 scissoring and the CSO antisymmtric

stretching vibrations, respectively. However, in the spectrum of D_2CSO no prominent bands were observed in this region.

IR spectrum of H_2CSO and D_2CSO were observed giving strong absorptions in the 1200-1150 cm^{-1} region. In the former case, three absorptions were observed at 1164, 1158 and 1151 cm^{-1}, the band at 1164 cm^{-1} was assigned to the S=O stretch. In the second case, two strong bands were observed at 1191 and 1181 cm^{-1} and the stronger band at 1181 cm^{-1} was assigned to υ_4 of D_2CSO. Very weak absorption at 818 cm^{-1} is assigned to CH_2 rocking. While, CH_2 wagging modes have been strongly observed bands at 765 cm^{-1} of H_2CSO and 607 cm^{-1} of D_2CSO. The bands at 397 and 345 cm^{-1} were assigned to the CSO bending modes of H_2CSO and D_2CSO, respectively. The band at 972 cm^{-1} was assigned to the C=S stretch of sulfine, and the band at 845 cm^{-1} was assigned to D_2CSO. Then, the bands at 860 and 719 cm^{-1} were assigned to the CH_2 and CD_2 rocking modes, respectively[32].

D. LAE JOO et al.[33] recorded the high-reslution FTIR spectrum of the υ_8 band of sulfine, H_2CSO, and analyzed the rotational structure in detail. They found the band υ_8 of sulfine is ideally suited for the study of an interacting bright and dark state in a transient molecule, also it is not overlapped by the bands from the multitude of the side products generated in the pyrolysis of dimethyl sulfoxide. The ground state constants derived from the combined fit of microwave and infrared data are

in improvement over previous values, including well-determined values for all the sextic centrifugal distortion constants.

1.1.2. NMR SPECTRA

The structure of dimesityl sulfine in solution and in the solid state was determined by NMR spectroscopy and X-ray crystallography, respectively. In the crystal, the two mesityl groups are twisted by approximately 60 °, while in solution an averaged conformation with C_s symmetry is observed, with anti mesityl ring located in the C=S=O plane and the syn mesityl ring perpendicular to the C=S=O plane[25,26]. In ^{1}H-NMR spectrum at -40°C the six methyl groups exhibit five singlets between δ=1.79 and 2.67. A singlet at δ=2.17 corresponds to two methyl groups. In the region of the aromatic protons only three singlets are found for the meta-protons, one signal (δ=6.91) corresponding to two protons. This shows that the two mesityl rings are not freely rotating and that the molecule possesses an average C_s symmetry under these conditions. Because of the non linearity of the group C=S=O, the two mesityl groups are nonequivalent[26].

^{13}C Spectrum of dimesityl sulfine displays at ambient temperature a number of the broad signals that sharpen on cooling, eventually yielding, below -30°C, five lines for the mesityl, three lines for the CH, and seven lines for the quaternary ring carbons[25]. The NMR spectrum of

4,4-disubstituted diphenyl sulfines were discussed in terms of the deshielding effect of the bent CSO system on the ortho- and meta-protons of either phenyl rings, this data revealed that :

a)-The deshielding effect of the CSO group is directed to one side of the molecule and is mainly caused by the S=O part rather than by the C=S moiety.

b)-The NMR spectrum of diphenyl sulfine shows absorptions corresponding to two protons at considerable lower field than the remaining eight protons. Hence, the bent CSO group directs its deshielding effect only to one side of the molecule.

c)-The values of substituent constant S· of the CSO group indicate that the deshielding effect on H-1 and H-5, the ortho protons decreases with electron with-drawing substituents and increases with electron releasing substituents, presumable because of their effect on the electron density in the CSO group[23].

^{13}C NMR signals of the sulfinyl carbon were evidenced for sulfine (R1R2CSO) where (R1 = iso-pr, R2 = SMe) at 200 ppm for the E-isomer and 204 ppm for the Z-isomer. In the proton spectra, the presence of both isomers was revealed by double sets of signals: for instance a methylthio group at 2.4 ppm for E-isomer and 2.5 ppm for the Z-one. Ratio was found to be 70:30[34].

Two isomeric Z- and E-forms of thioacrolein S-oxide were analyzed by ^{1}H NMR at -60°C. Also, the ^{13}C NMR spectrum showed the following peaks for (Z-isomer) 172.4 (CSO), 125.2, 123.9 ppm; and for the (E-isomer) 181.5 (CSO), 125.5, 124.9 ppm[35]. The C=S=O group was characterized by ^{13}C NMR in the range of 176 to 196 ppm for E-sulfines yielded from oxidation of dithiocarbamates[36].

Symmetric aliphatic sulfine formed from oxidation of symmetric aliphatic thioketone exhibited NMR signals that are characterisitic of sulfines (R1R2CSO), where (R1, R2 = iPr, n-C_6H_{13}) :

1)-large upfield shift of protons located at α-carbon and trans to the C=S group.

2)- The ^{13}C shifts of C=S=O are observed at 220 ppm[37].

1.2. THEORETICAL STUDIES

J. Lierop et al.[27] performed molecular orbital calculations for the parent sulfine and some mono- and dihalogen substituted sulfines, using ab initio and INDO methods. A partial geometry optimization was performed for nine different sulfines. They calculated charge distributions, potential surfaces and dipole moments from the wave functions of the optimized geometries, also cis-trans interconversion barriers and electronic spectra were presented. They found atomic charges of the S and O atoms are insensitive to substitutions at carbon atom. On the other hand,

geometry optimization of the different sulfines are not influenced by the substituents, the C-S bond length was taken to be 1.63 A° , r(S-O) was fixed at 1.47 A° , and substituents greatly influence the potential environment of the molecule by drawing isopotentail curves of sulfines. Finally, it is concluded that, the substituents at carbon must play a very important role in the outcome of nucloephilic or electrophilic substitution reactions of sulfines.

Dennis and James[31] examined assignments of the vibration fundamentals of sulfine (H_2CSO) both experimentally and theoretically. Ab initio predications of the fundamental vibrational frequencies, their relative intensities and their potential energy distributions show that the previous vibrational numbering and descriptions of the vibrations must be revised. These predications were confirmed by observations of the gas phase spectra of H_2CSO and D_2CSO. Also, this examination included a study of the structure of sulfine and they found that in order to adequately reproduce the experimental ground state geometry different calculations by using various basis sets must be performed. As an aid to assigning the spectra of fully deuterated and partially deuterated sulfine, they calculated the vibrational frequencies of these species at the MP2/6-311+G (2df,p) level and the results showed in both HDCSO and D_2CSO the most intense band is the CSO symmetric stretch, followed by the CHD (CD_2) out-of-plane wagging mode.

Sulfine and sulfine-D_2 have been generated by the pyrolysis of trans-1,3-dithietane 1,3-dioxide and its deuterated species, respectively, at 600 K and trapped in argon matrices at 20 K. The IR spectra of the pyrolysis products have been recorded in the 4000-250 cm^{-1} region at 10 K. The IR absorptions due to sulfine and sulfine-D_2 have been identified by their disappearance on subsequent irradiation of the matrices. Vib-rational assignments of sulfines have been made, referring to the freq-uencies predicted by ab initio MO calculations. Normal coordinate ana-lysis has been carried out for the in-plane modes of À species[32].

Theoretical methods were used to predict the UV/VIS spectral features of the sulfine compounds. The two lowest-energy n-π^* and π-π^* transitions type of the parent sulfine were predicted at different levels of theory, such as CASSCF/CASPT2, EOM-CCSD, CIS, TD-HF and TD-DFT. While calculations by singles-only configuration inter-action (CIS) and by radom phase approximation (TD-HF) methods provided too large transition energies, results obtained by time-dependent density-functional theory (TD-DFT) are close to those of the multi-configurational CASPT2 method. To characterize the sulfine chromo-phore, the sulfines of thiopropanal, thioacetone, 2,2̀,4,4̀-tetramethyl-1,3-thioxocyclobutanone, thioadomantanone, thiocyclopropenone, thiocyclo-pentadienone, thio-cycloheptatrienone, 4,4̀-dimethylthiobenzaphenone and thiofluorenone were calculated by the TD-DFT method[30].

R. Arnaud et al.[38] investigated the dimerization mechanism of the parent sulfine using hybrid DFT method (B3LYP) with a large basis set on the sulfur atom. Single-point post-HF calculations up to the CCSD(T) level were performed for some representative stationary points of the potential energy surface. They found six dimmers can be formed from the parent sulfine by different ways. The five membered rings formed by (2+3) cycloadditions (1,3-dipolar cycloadditions), while the four membered rings result from head-to-head and head-to-tail (2+2) cycloadditions. In the case of six membered rings (3+3) cycloadditions would be involved. The (2+3) mechanism was predicted to be the lowest energy pathway, with an activation barrier of 12.3 kcal/mol; the bond formation process is very asynchronous (in the first stage of the reaction, the C-C bond formation is more advanced than the S-O one) and probably a stepwise mechanism occurs involving a biradical intermediate. The alternative pathway involving an anti transition structure occurs with activation energy equal to 13.7 kcal/mol and is slightly less favorable. In both cases, the obtained cycloadduct is the five membered ring.

Gas-phase thermochemical properties of sulfine (H_2CSO) and the potential energy surface of its protonation process were studied by the density functional method (DFT) employing different exchange correlation potentials. All calculations showed that the stable protonated isomer is planar with the proton bonded to the oxygen atom in a trans

arrangement of the skeleton. Three transition states were located that allow interconversion between the different isomers. Hardnesses and Fukui indices were calculated to follow the reactivity trend along the protonation path and to explain the preference for particular protonation site on neutral sulfine. Good agreement between density functional theory and previous high-level theoretical and experimental data was also found for the heat of formation of sulfine and its most stable protonated form[29].

The heat of formation ΔH_f of the parent sulfine, has been determined theoretically by different methods for example, Ruttink et al.[1] used ab initio calculation at the level CAS-SDCI/CASSCF/DZ (2df,2d,p) + f(s) of theory. The CBS-QB3 quantum chemical method[39], Density functional theory (DFT) were successfully used to study the heat of formation of parent sulfine[40,41]. Ventura et al.[42] used density functional (DFT) level to solve the discrepancy between different theoretical values. In agreement with the CBS-QB3 calculations, which predict a value of -30 ± 61 KJ/mol, DFT calculations on isodesmic reactions predict a value of -38 ±10 KJ/mol. Previous estimation of -9 ±14 KJ/mol (at the MO level) and -52 ± 10 KJ/mol (at the DFT level) are discussed and shown to be artifacts of the methods of calculation employed.

A. Tangerman and B. Zwanenburg[24] presented an NMR study about restricted rotation of the aryl group around C-C bond of mesityl substituted sulfines in E- and Z-isomers. They found coalescence of the two methyl signals to one singlet was indeed observed for the Z- and E-sulfoxide sulfines at elevated temperatures. During this NMR analysis no Z- to E- (or visa versa) isomerization was observed. The rotational barrier around C-C bond in the Z-form is smaller than in the E-form. And also, in the E-form the barrier to rotation is only slightly affected by the substituent R for R being phenyl, α-thienyl and β-naphthyl, when R being the less bulky aliphatic ethyl group the value of rotational barrier was about 1.5 kcal/mol or less.

E. Block et al.[28] used Restricted Hartree-Fock (RHF) level with a variety of basis sets and employed both a rigid and non-rigid rotor model for the CH_3-rotation of ethanethial S-oxide (CH_3CHSO) which show syn (Z) form to be more stable than the anti (E) form by 1.7 kcal/mol. That agrees with experimental result (microwave study of ethanethial S-oxide, the only conformation observed is the syn form). The conformational preference for structure of CH_3CHSO can be explained in terms of orbital and electrostatic interactions between the terminal oxygen and methyl hydrogen atoms which are negligible in the anti form.

The rotation for two isomeric (Z- and E-) of thioacrolein S-oxide around C-C single bond was studied theoretically by using HF/6-31+G*

level, MP2/6-31+G* level, QCISD(T)/6-31+G* level. In Z-form, rotation around the C-C single bond gives a cyclic isomer (five membered ring) which has lower energy than Z-thioacrolein S-oxide. However, this rearrangement was calculated to run via a relatively high energy TS. The cyclic isomer (four membered ring) results from the rearrangement of E-thioacrolein S-oxide, here also after rotation around the C-C single bond[35].

On the other hand, magnetic properties: rotational Zeeman effect of the parent sulfine and a new MWFT set-up for on-line pyrolysis studies were discussed by A. Klesing and D. Sutter[43]. Based on experimentally determined diagonal elements for the molecular g-tensor and two anisotropies of the magnetic susceptibilities, they derived the anisotropies of the second electronic moments and the diagonal elements of the molecular quadruple moment tensor species with high accuracy. These data were used to check the quality of moderately sized ab initio calculations aiming at the vibronic ground state, and subsequently to gain an insight into the shielding behavior of sulfine. Although they found sulfine to be less demanding than sulfur dioxide. It was suggested that further experimental and theoretical studies on this compound would be of great value. They quote only values for the magnetic susceptibilities as obtained by the IGLO method.

1.3. SULFINE COMPLEXES

Sulfine complexes of palladium and platinum $(Ph_3P)_2M(R^1R^2CSO)$ (M = Pd, Pt; R^1R^2C = fluorenylidene; R1 = 2-methoxy-1-naphthyl, R2 = H) have been obtained by reaction of $(Ph_3P)_2ML_2$ (L_2 = $(PPh_3)_2$, C_2H_4) with sulfines. The platinum fluorenylidene sulfine complex could be prepared also from $(Ph_3P)PtSO_2$ and 9-trimethyl silyl fluorenylithium. Infrared, ^1H, ^{13}C and ^{31}P NMR spectra showed that the sulfine are bonded through the carbon sulfur atoms[21]. While, reaction of $Pt(PPh_3)_4$ with sulfines, XYCSO, (X, Y = aryl, S-aryl, S-alkyl, Cl) yield coordination compounds of the type $Pt(PPh_3)_2(XYCSO)$. Infrared, ^{31}P and ^1H NMR spectra revealed that in all cases the sulfine ligand is coordinated side-on via the C=S π-bond (Pt-η^2-CS). Also, reactions of $Pt(PPh_3)_4$ with either the E- or Z-isomer of $(p\text{-}CH_3C_6H_4)(CH_3S)CSO$ yields the corresponding E- or Z-coordination compound indicating that the configuration of the sulfine ligand is retained upon coordination to the $Pt(PPh_3)_2$ unit[20].

In more recent work, the electron-rich thioformaldehyde complex, $OSCl(NO)(CH_2S)(PPh_3)_2$ is oxidized by 3-chloroperbenzoic acid at the sulfur atom to give the first example of a complex containing the unsubstituted sulfine, H_2CSO[44]. N. Kuhnert et al.[14] synthesized sulfine complexes by oxidation of thioaldehyde complexes, SO transfer to a carbene complex, as well as methylene transfer to a complex of sulfur monoxide and also they studied the dynamic behavior of these complexes.

1.4. SYNTHESIS AND ISOMERIZATION

Walter[45] prepared thioamide S-oxide by oxidation of thioamide using hydrogen peroxide. Also Shappard and Dieckmann[46] synthesized fluorenethione S-oxide by Dehydrochlorination reaction of the corresponding sulfinyl chloride. The parent sulfine (H_2CSO) was prepared as a product of pyrolysis of dimethyl sulfoxide (DMSO)[43,31].

The stereo of the product sulfine (E- or Z-configuration) depends on the method of preparation and the type of R1, R2 groups attached to the carbon atom of sulfine group (R1R2CSO). Treatment of diaryl thio-ketone with dimethyl dioxirane (DMDO) produced sulfines in high yield, for example mesityl phenyl thioketone gave an E:Z mixture of sulfine in the ratio 7:3. The modified Peterson reaction involving the reaction of α-silyl carbanions with sulfur dioxide is a very attractive to produce diffe-rent sulfines[47].

D. Chevrie et al.[36] and A. Le NOCHER et al.[37] employed oxidation reaction of various dithiocarbamates, enethiolizable symmetric, unsymmetric aliphatic thioketone with standered oxidizing agent, meta-chloroperbenzoic acid (mCPBA), to give E-sulfines, respectively. Oxidation of 2,4,6-tri-t-butylthiobenzaldehyde with (mCPBA) or (DMDO) gives a mixture of E- and Z-thioaldehyde oxides with different ratios[10].

Unsaturated sulfine (thioacrolein S-oxide) was synthesized by flash vacuum thermolysis (FVT) of sulfoxide (as a mixture of two isomers Z/E) at 600°C, where in case of dimethyl anthracene, the ratio of Z/E of product sulfine was 78/22[35].

1.5. SULFINE REACTIONS

G. Mazzanti et al.[48,49] studied an intramolecular cyclization of (allyl sulfanyl) sulfines via their vinyl sulfenic acid tautomers. Several studies for different sulfines were performed:

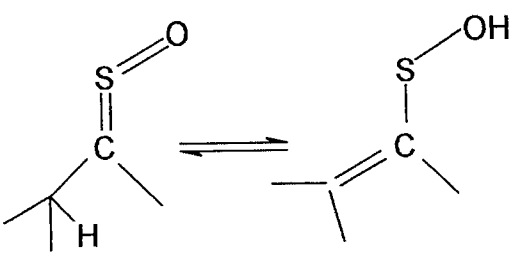
1-Thermal intramolecular cyclization of enethiolisable (allyl sulfanyl) sulfines in toluene affords 2-alkylidene-1,3-dithiolane 1-oxides.

2-Also, sulfines having an S-(prop-2-ynyl) substituent gave 2-alkylidene-5-methylene-1,3-dithiolane 1-oxides.

3-The formation of such compounds was explained by an initial tautomerization of the sulfine to vinyl sulfenic acid, followed by an intramolecular addition of the sulfenic acid to the allylic double bond.

4-The intramolecular reaction of (allyl sulfanyl) sulfines in presence of thionyl chloride gave the cyclic product. While, the reaction of prop-2-ynyl sulfanyl substituted sulfine with thionyl chloride gave only brown tars, but at low reaction temperature gave only a 13% of sulfenyl chloride.

They concluded that sulfines having a hydrogen atom at the α-carbon atom, show the propensity to undergo enethiolization to the corresponding vinyl sulfenic acids[48,50], provided suitable conditions are chosen. Usually, the tautomeric equilibrium is at the sulfine side (**A**). However, when the vinyl sulfenic acids **B** are transformed into a derivative by an irreversible reaction the equilibrium is shifted to the right-hand side (**B**).



(A) **(B)**

Information about the ease of the tautomeric interconversion can be obtained by investigating the optical integrity of chiral sulfines having a sterogenic center at C-α was achieved[47].

1.5.1. CYCLIZATION AND CYCLOADDITION REACTIONS

The most frequently used reaction of sulfines is the Diels-Alder type cycloaddition with 1,3-diene to give dihydrothiopyrane S-oxides. Asymmetric Diels-Alder reactions have been studied in details[47].

Thioketone S-oxide (sulfines) undergo cycloaddition reaction with a variety of 4π-electron systems such as 1,3-dienes and 1,3-dipoles. In all

cases the carbon-sulfur bond in these heterocumlenes takes part in the cycloaddition process.

Diaryl thioketone S-oxides reacts with the 2H-azirine in the presence of boron trifluoride diethyl ether to give the oxathiozines via a 1,3-cyclization across the sulfine C=S=O bond[51]. The α-oxo-sulfine acts as diene component in [4+2] cycloaddition reaction with simple alkenes or alkynes to give 2H-3-thiapyran fused heterocyclic[52]. 1,3-Dipolar cycloadditions of aromatic sulfine (thiobenzophenone S-oxide) with 2,2,4,4,-tetramethyl-3-thioxocyclobutanone afforded the spiro 1,2,4-trithiolane (86% yield)[53].

1.5.2. DECOMPOSITION OF SULFINES

Generally, loss of the sulfur atom and formation of a carbonyl compound is the major route for the sulfine decomposition[26]. Thermally allowed electrocyclization of sulfines leads to the corresponding ketone by forming of intermediate oxathiiranes followed by sulfur extrusion[37]. Trithioperester sulfines compounds undergo at room temperature a novel rearrangement to acyltrisulfides by the following pathway: electrocyclization to an intermediate oxathiirane, opening of this three membered ring (oxathiirane) with migration of the alkyldithio group to afford acyltrisulfides[34].

1.5.3. CARBOPHILIC, THIOPHILIC REACTIONS

A thiophilic attack of dithioester sulfine which reacts with amine gives a thione-S-imide and hence dimerizes to cyclic sulfonamide after proton transfer and N-S bond rearranges yielding the thiooxamates. A carbophilic addition was suggested for the reaction with secondary amines[18,19,54].

CHAPTER TWO

THEORETICAL BACKGROUND

2.1. AB-INITIO METHODS

The term "ab-initio" implies that within the frame of a particular variation or perturbation method no approximations are adopted, though the method itself is a mere approximation to the solution of Schrödinger equation. That means that, unlike in semiempirical methods, no integrals are neglected or approximated by simplified expressions and functions containing empirical parameters, or even replaced by empirical parameters. Explicit inclusion is also made for inner shell electrons. All integrals should be calculated with a high accuracy. "Ab-initio" also implies that a nonrelativistic Hamiltonian within the Born Oppenheimer approximation is used.

2.1.1. THE SCHRÖDINGER EQUATION

According to quantum mechanics, the energy and many properties of a stationary state of a molecule can be obtained by solution of the Schrödinger partial differential equation[55].

$$\hat{H}\,\Psi = E\,\Psi \qquad (1)$$

$\hat{H}$ is the Hamiltonian, a differential operator representing the total energy. E is the numerical value of the energy of the state, and Ψ is the wave

function. It depends on both cartesian and spin coordinates of all particles. The Hamiltonian $\hat{H}$, is the sum of kinetic and potential parts,

$$\hat{H} = \hat{T} + \hat{V} \tag{2}$$

Where: $\hat{T} = -\frac{h^2}{8\pi^2}\sum_i \frac{1}{m_i}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right)$ (3)

The sum is overall particles i (nuclei and electrons), m_i is the mass of particle i, h is Plank`s constant.

The potential energy operator is the coulomb interaction:

$$\hat{V} = \sum_i \sum_{j<} \frac{(e_i\, e_j)}{r_{ij}} \tag{4}$$

Where the sum is over distinct pairs of particles (i, j) with electric charges e_i, e_j separated by a distance r_{ij}.

Within the Born–Oppenheimer approximation[56] equation (1) may be written as:

$$\hat{H}^{elec}\ \psi^{elec}_{(r,R)} = E^{eff}_{(R)}\ \psi^{elec}_{(r,R)} \tag{5}$$

The main task is to solve, at least approximately, the electronic Schrödinger equation (5), and hence find the effective nuclear potential function E_r^{eff}.

2.1.2. MOLECULAR ORBITAL THEORY

It is an approach to molecular quantum mechanics, which uses one-electron functions or orbitals to approximate the full wavefunction. A molecular orbital, $\psi(x,y,z)$, is a function of the cartesian and spin coordinates of a single electron.

A full antisymmetric many-electron molecular orbital wave-function for the closed-shell ground state of a molecule with n (even) electrons, can be written down as:

$$\Psi = (n!)^{-1/2} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1)\cdots\cdots & \psi_{\frac{n}{2}}(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2)\cdots\cdots & \psi_{\frac{n}{2}}(2)\beta(2) \\ \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots \\ \psi_1(n)\alpha(n) & \psi_1(n)\beta(n) & \psi_2(n)\alpha(n)\cdots\cdots & \psi_{\frac{n}{2}}(n)\beta(n) \end{vmatrix} \qquad (6)$$

This determinant is referred to as a Slater determinant[57].

2.1.3. BASIS SET EXPANSIONS

A further restriction is imposed, requiring that the individual molecular orbitals be expressed as linear combinations of a finite set of N

prescribed one-electron functions known as basis functions ϕ_μ. Then an individual orbital ψ_i can be written:

$$\psi_i = \sum_{\mu=1}^{N} c_{\mu i}\phi_\mu \qquad (7)$$

Where $c_{\mu i}$ are the molecular orbital expansion coefficients, these coefficients provide the orbital description with some flexibility.

In simple qualitative versions of molecular orbital theory, atomic orbitals of constituent atoms are used as basis functions. Such treatments are described as linear combination of atomic orbital (LCAO) theories. There are two types of atomic basis functions. The first one is Slater-type atomic orbitals (STO`s), which have exponential radial parts. They are labeled like hydrogen atomic orbitals 1s, 2s, $2p_x$. The second type of basis consists of gaussian-type atomic functions. These are powers of x, y, z multiplied by exp ($-\alpha r^2$), $\alpha$ being a constant determining the size. GTO`s functions were introduced into molecular orbital computations by Boys[58]. They are less satisfactory than STO`s as representations of atomic orbitals. Nevertheless, they have the important advantage that all integrals in the computations can be evaluated explicitly without recourse to numerical integration.

A third possibility is to use linear combinations of gaussian functions as basis functions. For example, an s-type basis function.

$$\phi_\mu = \sum_s d_{\mu s} g_s \ . \qquad (8)$$

The coefficients $d_{\mu s}$ are fixed. Basis functions of this type are called contracted gaussians; the individual g_s being termed primitive gaussians.

2.1.4. TYPES OF BASIS SETS

Minimal Basis Sets – The STO-nG Basis Sets:

The STO-nG[59] is a Slater-type orbitals simulated by n Gaussian functions each STO-3G is a minimal basis set because it has only as many orbitals as are necessary to accommodate the electrons of the neutral atom. The main problem of any minimal basis set is its inability to expand or contract its orbitals to fit the molecular environment. One solution to the problem is to use split-valence or double-zeta basis sets.

2.1.4.1. SPLIT-VALENCE AND DOUBLE-ZETA BASIS SETS

In this basis, the atomic orbitals are split into two parts, an inner, compact orbital and an outer, more diffuse one. The coefficients of these two types of orbitals can be varied independently during constructions of the molecular orbitals in the SCF procedure. Double-zeta basis set is

another type of split basis sets. It splits core orbitals as well as valence orbitals, whereas, split-valence basis sets split only valence orbitals. 6-31G[60] is an example of the split-valence basis sets. It means that the core orbitals consist of six and the inner and outer valence orbitals of three and one gaussian functions, respectively.

2.1.4.2. POLARIZATION BASIS SETS

This type of basis sets incorporates functions of higher angular quantum number than are needed by the atom in its electronic ground state. It provides for displacement of electronic charge away from the nuclear centers, that is, charge polarization.

a) The 6-31G* and 6-31G** Polarization Basis Sets[61-62]

6-31G* basis set is constructed by the addition of a set of six second-order (d-type) gaussian primitives to the split-valence 6-31G basis set for the description of each heavy (non-hydrogen) atom. A more complete basis set termed 6-31G**, has been constructed. It is identical to 6-31G* except for the addition of a set of gaussian p-type functions to each hydrogen and helium atom.

b) The 6-311G** Basis Sets [63]

Although they are more flexible than the simple 6-31G* and 6-31G** polarization basis sets, their size has limited their application to only quite small molecular systems. The 6-311G** comprises an inner

shell of six s-type gaussians and an outer (valence) region, which has been split into three parts, represented by three, one, and one primitive, respectively. The basis set is supplemented by a set of five d-type gaussians for hydrogen. The 311G "triple" split increases the overall flexibility of the basis set and improves the description of the outer valence region.

2.1.5. VARIATIONAL METHODS AND HARTREE-FOCK THEORY

Up to this point, it has been described how a determinant wave function may be constructed from molecular orbitals, and how the orbitals may, in turn, be expanded in term of a set of basis functions. It remains to specify a method for fixing the coefficients. This is the Hartree-Fock theory[64]. It is based on the variational method in quantum mechanics[65].

The variational method may be applied to determine optimum orbitals in single-determinant wave functions. For a particular molecular orbital, Ψ_i, where,

$$\Psi_i = \sum_{\nu} C_{i\nu}\phi_{\nu} \,. \tag{9}$$

The coefficients $c_{\mu i}$ may be adjusted to minimize the expectation value of the energy E`. The resulting value of E` will then be as close to the exact energy E as is possible within the limitations imposed by:

a) The single-determinant wavefunction,

b) The particular basis set employed. And

C) Hence the best single determinant wavefunction is found by minimizing E` with respect to the coefficients $c_{\mu i}$. This implies the variational equations

$$\frac{\partial E`}{\partial c_{\mu i}} = 0.0 \quad (\text{all } \mu, i) \tag{10}$$

2.1.5.1. CLOSED-SHELL SYSTEMS

The variational condition (10) leads to a set of algebraic equations for $c_{\mu i}$. They were derived independently for the closed-shell wavefunction (6) by Roothaan[66] and by Hall[67]. The Roothaan-Hall equations are:

$$\sum_{\nu=1}^{N}(F_{\mu\nu} - \varepsilon_i S_{\mu\nu})c_{\nu i} = 0 \qquad . \ \mu = 1,2,\ldots,N \tag{11}$$

with the normalization conditions

$$\sum_{\mu=1}^{N}\sum_{\nu=1}^{N} c^*_{\mu i} S_{\mu\nu} c_{\nu i=1} \ . \tag{12}$$

Here, ε_i is the one-electron energy of molecular orbital ψ_i, $S_{\mu\nu}$ are the elements of an $N \times N$ matrix termed the overlap matrix,

$$S_{\mu\nu} = \int \phi_\mu^*(1)\, \phi_\nu(1)\, dx_1\, dy_1\, dz_1 \,. \tag{13}$$

and $F_{\mu\nu}$ are the elements of another $N \times N$ matrix termed the Fock matrix,

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^{N}\sum_{\sigma=1}^{N} P_{\lambda\sigma}\left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)\right] \tag{14}$$

$H_{\mu\nu}^{core}$ is a matrix representing the energy of a single electron in a field of "bare" nuclei. Its elements are

$$H_{\mu\nu}^{core} = \int \phi_\mu^*(1)\, \hat{H}^{core}(1)\, \phi_\nu(1)\, dx_1\, dy_1\, dz_1 \,. \tag{15a}$$

$$\hat{H}^{core}(1) = -\frac{1}{2}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) - \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \,. \tag{15b}$$

Here Z_A is the atomic number of atom A, and summation is carried out over all atoms. The quantities $(\mu\nu|\lambda\sigma)$ are two-electron repulsion integrals:

$$(\mu\nu|\lambda\sigma) = \iint \phi_\mu^*(1)\phi_\nu(1)\left(\frac{1}{r_{12}}\right)\phi_\lambda^*(2)\phi_\sigma(2)\, dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \,. \tag{16}$$

They are multiplied by the elements of the one-electron density matrix. $P_{\lambda\sigma}$.

$$P_{\lambda\sigma} = 2\sum_{i=1}^{occ} c_\lambda c_{\sigma i}^* \,. \tag{17}$$

The summation is over occupied molecular orbitals only. The electronic energy is given by:

$$E^{ele} = \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N} P_{\mu\nu}(F_{\mu\nu} + H_{\mu\nu}^{core}) \qquad (18)$$

Which when added to the internuclear repulsion, E^{nr},

$$E^{nr} = \sum_{A}^{M}\sum_{B<} \frac{Z_A Z_B}{R_{AB}} \qquad (19)$$

an expression for the total energy is obtained.

The Roothaan-Hall equations are not linear since the Fock matrix $F_{\mu\nu}$ itself depends on the molecular orbital coefficient, $c_{\mu i}$, through the density matrix, $P_{\lambda\sigma}$.

2.1.5.2. OPEN –SHELL SYSTEMS

For open-shell systems, the Roothaan-Hall equations need modifications. Simple molecular orbital theory can be extended to open –shell systems in two possible ways. The first is described as spin-restricted Hartree-Fock (RHF) theory[68]. In this approach, a single set of molecular orbitals is used, some being doubly occupied and some being singly occupied with an electron of α spin. The coefficients $c_{\mu i}$ are still defined by the expansion (9) and their optimum values are still obtained from the variational conditions, (10).

The second type of molecular orbital theory in common use for open-shell systems is spin-unrestricted Hartree-Fock (UHF) theory[69]. In this approach, different spatial orbitals are assigned to α and β electrons. Thus, there are two distinct sets of molecular orbitals ψ_i^{α} and ψ_i^{β} (i= 1,...,N). Since the RHF function is a special case of the UHF function, it follows from the variational principle that the optimized UHF energy must be below the optimized RHF value. UHF functions have the disadvantage that they are not true eigenfunctions of the total spin operator. Thus, UHF wave functions, which designed for doublet states, are contaminated by functions corresponding to states of higher spin multiplicity, such as quartets.

In UHF theory, the two sets of molecular orbitals are defined by two sets of coefficients,

$$\psi_i^{\alpha} = \sum_{\mu=1}^{N} c_{\mu i}^{\alpha} \phi_{\mu}; \qquad \psi_i^{\beta} = \sum_{\mu=1}^{N} c_{\mu i}^{\beta} \phi_{\mu}. \tag{20}$$

These coefficients are varied independently, leading to the UHF generalizations of the Roothaan-Hall equations[70]. These are

$$\sum_{\nu=1}^{N} (F_{\mu\nu}^{\alpha} - \varepsilon_i^{\alpha} S_{\mu\nu}) c_{\mu i}^{\alpha} = 0 \tag{21}$$

$$\sum_{\nu=1}^{N} (F_{\mu\nu}^{\beta} - \varepsilon_i^{\beta} S_{\mu\nu}) c_{\mu i}^{\beta} = 0 \qquad \mu = 1,2,...,N. \tag{22}$$

Hence, the two Fock matrices are defined by:

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^{N}\sum_{\sigma=1}^{N}\left[(P_{\lambda\sigma}^{\alpha} + P_{\lambda\sigma}^{\beta})(\mu\nu|\lambda\sigma) - P_{\lambda\sigma}^{\alpha}(\mu\lambda|\nu\sigma)\right]. \tag{23}$$

$$F_{\mu\nu}^{\beta} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^{N}\sum_{\sigma=1}^{N}\left[(P_{\lambda\sigma}^{\alpha} + P_{\lambda\sigma}^{\beta})(\mu\nu|\lambda\sigma) - P_{\lambda\sigma}^{\beta}(\mu\lambda|\nu\sigma)\right]. \tag{24}$$

The density matrix is also separated into two parts.

$$P_{\mu\nu}^{\alpha} = \sum_{i=1}^{\alpha occ} c_{\mu i}^{\alpha *} c_{\nu i}^{\alpha}; \qquad P_{\mu\nu}^{\beta} = \sum_{i=1}^{\beta occ} c_{\mu i}^{\beta *} c_{\nu i}^{\beta}. \tag{25}$$

The integrals $S_{\mu\nu}, H_{\mu\nu}^{core}$ and $(\mu\nu|\lambda\alpha)$ are the same as those already defined in the Roothaan-Hall procedure for closed shell calculations.

2.1.6. MULLIKEN POPULATION ANALYSIS

The electron density functions, $\rho(r)$, is a three-dimensional function defined such that $\rho(r)dr$ is the probability of finding an electron in a small volume element, dr, at some point in space, r- Normalization requires that

$$\int \rho(r)dr = n \tag{26}$$

where n is the total number of electrons.

For a single-determinant wavefunction, $\rho(r)$ is given by

$$\rho(r) = \sum_{\mu}^{N}\sum_{\nu}^{N} P_{\mu\nu}\phi_{\mu}\phi_{\nu} \tag{27}$$

where $P_{\mu\nu}$ are elements of the density matrix (17).

Allocating the electrons in some fractional manner among the various parts of a molecule (atoms, bonds, etc.) is useful to define the

total electronic charge on a particular atom in a molecule. This may imply a quantitative meaning to concepts as electron withdrawing or donating ability. This is done by what is called Mulliken Population Analysis. Integration of eq. (27) leads to

$$\int \rho(r)dr = \sum_{\mu}^{N}\sum_{\nu}^{N} P_{\mu\nu}S_{\mu\nu} = n \qquad (28)$$

where $S_{\mu\nu}$ is the overlap matrix. The total electron count is thus composed of individual terms $P_{\mu\nu}S_{\mu\nu}$. Given that ϕ_μ are normalized i.e., $S_{\mu\mu} = 1$, the diagonal terms in (28) are just $P_{\mu\mu}$ (the number of electrons directly associated with ϕ_μ). This is termed the net population of ϕ_μ. The off diagonal components occur in pairs, $P_{\mu\nu}S_{\mu\nu}$ and $P_{\nu\mu}S_{\nu\mu}$, of equal magnitude. Their sum,

$$Q_{\mu\nu} = 2P_{\mu\nu}S_{\mu\nu} \qquad (\mu \neq \nu), \qquad (29)$$

is referred to as an overlap population. The total electronic charge is now partitioned into two parts; the first associated with individual basis functions, the second with pairs of basis functions:

$$\sum_{\mu}^{N} P_{\mu\mu} + \sum_{\mu}^{N}\sum_{\nu<}^{N} Q_{\mu\nu} = n. \qquad (30)$$

It is sometimes desirable to partition the total charge among only the individual basis functions. One way this may be accomplished is to divide the overlap populations $Q_{\mu\nu}$, equally between the basis functions

ϕ_μ and ϕ_ν, adding half to each of the net population $P_{\mu\mu}$ and $P_{\nu\nu}$. This gives a gross population for ϕ_μ, defined as

$$q_\mu = P_{\mu\mu} + \sum_{\nu \neq \mu} P_{\mu\nu} S_{\mu\nu} . \tag{31}$$

The sum of gross populations for all N basis functions, ϕ_μ, is equal to the total electron count,

$$\sum_{\mu}^{N} q_\mu = n . \tag{32}$$

This is an arbitrary division of the overlap populations, $Q_{\mu\nu}$, into equal contributions from ϕ_μ and ϕ_ν.

The gross basis function populations may be used to define gross atomic populations:

$$q_A = \sum_{\mu}^{A} q_\mu . \tag{33}$$

The summation is carried out for all functions ϕ_μ on a particular atom, A. Finally, a total atomic charge on A may be defined as, where Z_A is the atomic number A. A total overlap population, q_{AB}, between two atoms A and B may be defined in a similar manner,

$$q_{AB} = \sum_{\mu}^{A} \sum_{\nu}^{B} Q_{\mu\nu} . \tag{34}$$

Here summation is carried out for all μ on atom A and all ν on atom B. Total overlap populations provide quantitative information about the binding between atoms.

2.1.7. MULTI-DETERMINANT WAVEFUNCTIONS

Up to this point, the theory has been developed in terms of single-determinant wavefunctions. It must be recognized that exact wave-function cannot generally be expressed as single determinants. The primary deficiency of Hartree-Fock theory is the inadequate treatment of the correlation between motions of electrons. In particular, single-determinant wavefunctions take no account of correlation between electrons with opposite spin. This leads to calculated (Hartree-Fock) energies that are above the exact values.

$$E\,(\text{exact}) = E\,(\text{Hartree-Fock}) + E\,(\text{correlation}). \qquad (35)$$

The neglect of correlation between electrons of opposite spin leads to a number of qualitative deficiencies in the description of electronic structure and energetics. There are two methods, will be briefly outlined, that address this problem. Both involve use of a linear combination of Slater determinants, each of which represents an individual electron configuration interaction.

2.1.7.1. FULL CONFIGURATION INTERACTION

Consider a system comprising n electrons described by a set of N functions, ϕ_μ. The ground state HF single-determinant wave function is

Ψ_0,

$$\Psi_0 = (n!)^{-1/2} |\chi_1 \chi \cdots \chi_n| . \qquad (36)$$

Determinantal wave functions, other than the HF function Ψ_0, may be constructed replacing one or more of the occupied spin orbitals $\chi_i, \chi_j, \ldots\ldots$ in (36) by virtual spin orbitals $\chi_a, \chi_b, \ldots\ldots$ The resulting determinants will be denoted as Ψ_s with s > 0. They may be further classified into single-substitution functions, ψ_i^a in which χ_i is replaced by χ_b, double-substitution functions, ψ_{ij}^{ab} in which χ_i replaced by χ_a and χ_j by χ_b, triple-functions and so forth. The general substitution determinant, $\Psi_{ijk\ldots\ldots}^{abc\ldots\ldots}$, with the restrictions i < j < k < .. .. and a < b < c < ..... to avoid repetition of the same configuration.

In the full configuration interaction method, a trial wavefunction,

$$\Psi = a_0 \Psi_0 + \sum_{s>0} a_s \Psi_s . \qquad (37)$$

is used, where the summation is overall substituted determinants. The unknown coefficients, a_s, are then determined by the linear variational method, leading to

$$\sum_s (H_{st} - E_i \delta_{st}) a_{si} = 0 \qquad t = 0,1,2,\ldots\ldots\ldots \qquad (38)$$

Here, H_{st} is a configurational matrix element,

$$H_{st} = \int \ldots \int \Psi_s H \Psi_t d\tau_1 d\tau_2 \ldots d\tau_n . \qquad (39)$$

And E_i is energy. Because the determinantal wavefunctions Ψ_s are mutually orthogonal, the overlap matrix S is replaced by a simple delta function, δ_{st}.

The full configuration interaction method represents the most complete treatment possible within the limitations imposed by the basis set. As the basis set becomes more complete, the result of a full configuration interaction treatment will approach the exact solution of the nonrelativistic Schrödinger equation. The full CI method is well defined, size –consistent and variational. However, it is not practical except for very small systems.

2.1.7.2. MOLLER-PLESSET PERTURBATION THEORY

The perturbation theory of Moller and Plesset[71], closely related to many-body perturbation theory, is an alternative approach to the correlation problem. Its aim is still to find the lowest eigenvalue and corresponding eigenvector of the full Hamiltonian matrix. The approach is not to truncate the matrix as in limited CI, but rather to treat it as the sum of two parts, the second being a perturbation on the first. Moller-Plesset models are formulated by first introducing a generalized electronic Hamiltonian, $\hat{H}_\lambda$, according to

$$\hat{H}_\lambda = \hat{H}_0 + \lambda \hat{V} . \qquad (40)$$

$\hat{H}_0$ is an operator such that the matrix with elements

$$\int\ldots\int \psi_s \hat{H}_0 \psi_t \, d\tau_1 \, d\tau_2 \ldots d\tau_n \tag{41}$$

is diagonal. The perturbation, $\lambda \hat{V}$, is defined by

$$\lambda \hat{V} = \lambda (\hat{H} - \hat{H}_0), \tag{42}$$

where $\hat{H}$ is the correct Hamiltonian and λ is dimensionless parameter. $\hat{H}_\lambda$ coincides with $\hat{H}_0$ if $\lambda = 0$, and with $\hat{H}$ of $\lambda = 1$ In MP theory, the zero-order Hamiltonian, $\hat{H}_0$, is taken to be the sum of the one-electron Fock operators. The eigenvalue E_s, corresponding to a particular determinant, ψ_s, is the sum of the one-electron energies, ε_i, for the spin orbitals which are occupied in ψ_s. ψ_λ and E_λ, the exact or full CI (within a given basis set) ground-state wavefunction and energy for a system described by the Hamiltonian $\hat{H}_\lambda$, may now be expanded in powers of λ according to Rayleigh-Schrödinger perturbation theory[72].

$$\psi_\gamma = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots \tag{43}$$

$$E_\lambda = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots \tag{44}$$

Practical correlation methods may now be formulated by setting $\lambda = 1$ and by truncation of the series in eq. (44) to various orders. It refers to the methods by the highest order energy term allowed, that is, truncation

after second-order as MP2, after third-order as MP3 and so forth. The leading terms in expansions (44) are

$$\psi^{(0)} = \psi_0 \tag{45}$$

$$E^{(0)} = \sum_{i}^{occ} \varepsilon i \tag{46}$$

$$E^{(0)} + E^{(1)} = \int \ldots \int \psi_0 \, \hat{H} \, \psi_0 \, d_{T_1} \, d_{T_2} \ldots d_{T_n} \tag{47}$$

Where ψ_0 is the HF wavefunction and ε_i are the one-electron energies. The MP energy to first-order is thus the HF energy. Higher terms in the expansion involve other matrix elements of the operator $\hat{V}$.

The first order contribution to the wavefunction is

$$\psi^{1)} = \sum_{s>0} (E_0 - E_s)^{-1} V_{so} \, \psi_s \tag{48}$$

where V_{so} are matrix elements involving the perturbation operator, $\hat{V}$,

$$\int \ldots \int \psi_s \, \hat{V} \, \psi_0 \, d\tau_1 \, d\tau_2 \ldots d\tau_n \tag{49}$$

It follows that the first-order contribution to the coefficients as in equation (38) is given by

$$a_s^{(1)} = (E_0 - E_s)^{-1} V_{so} . \tag{50}$$

The second –order contribution to the Moller-Plesset energy is:

$$E^{(2)} = -\sum_{s}^{D} (E_0 - E_s)^{-1} |V_{so}|^2 \tag{51}$$

where $\sum^{D}$ indicates that the summation to be carried out overall double substitutions. This represents the simplest approximate expression for the correlation energy. If ψ_s is the double substitution $i\,j \rightarrow a\,b$, the expression for V_{so} is

$$V_{so} = (i\ j|\ |a\ b) \tag{52}$$

where $(i\ j|\ |a\ b)$ is a two.electron integral over spin orbitals, defined by

$$(i\ j|\ |a\ b) = \iint \chi\ i^*(1)\,\chi\, i^*(2)\,(\frac{1}{r_{12}})\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)]\,d\tau_1\,d\tau_2 \tag{53}$$

Here, integration is overall coordinates for both electrons. The final formula for the second-order contribution to the energy becomes

$$E^{(2)} = \sum_{i}^{OCC} \sum_{j} \sum_{a}^{virt} \sum_{b} (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)^{-1}\ |(ij|\ |ab)|^2 \tag{54}$$

Unlike the simple CID and CISD configuration interaction schemes, MP2 requires only a partial transformation of the two-electron integrals of equation (16) into a spin orbital basis.

The third-order contribution to the Moller-Plesset energy also follows directly from Rayleigh-Schrödinger theory. It is

$$E^{(3)} = \sum_{s}^{D} \sum_{t}^{D} (E_0 - E_s)^{-1}\ (E_0 - E_t)^{-1}\ V_{os}\ (V_{st} - V_{oo}\delta_{st})\ V_{to} \tag{55}$$

where the summations are again carried out over double substitutions only. The matrix elements V_{st} between different double substitutions require a full integral transformation or other techniques of comparable

complexity[73]. At the fourth-order of theory, single, triple, and quadruple substitutions also contribute, since they have nonzero Hamiltonian matrix elements with the double substitutions. The triple substitutions are the most difficult computationally, and some computations have been carried out using only singles, doubles, and quadruples. This partial fourth-order level of theory is termed MP4SDQ.

MP2, MP3, and MP4 energy expressions are well defined. They can be applied quite widely. They do satisfy the size-consistency requirement, as do Moller.Plesset energy expansions terminated at any order. This follows since full CI is size consistent with the Hamiltonian $\hat{H}_\lambda$ for any value of λ; hence, individual terms in equation (44) must be size-consistent. In this respect, the perturbation expressions are more satisfactory than the CID or CISD methods for determining correlation energies. On the other hand, perturbation theory results, terminated at any order, are no longer variational since they are not derived as expectation values of the Hamiltonian.

2.2. METHOD OF CALCULATIONS

All of molecules and conformers were fully optimized without any constrains. Three levels were used, viz; ab initio molecular orbital Hartree Fock (HF)[74], Müller Plesset (MP2)[71] and the density functional theory (B3LYP)[75,76], thus the electron correlation was put into consideration. Various of basis sets were used, 6-31G, 6-31+G*, up to 6-311+G**[63]. The polarization and diffuse functions were incorporated to deal with and describe the systems where electrons are relatively far from the nuclei, lone paris.

The nature of each stationary point was characterized by calculating the corresponding vibrational frequencies. The transition states are those imaginary frequency. The calculations were carried out using GAUSSIAN 94[77] and GAMESS 98[78] packages.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1. GEOMETRY

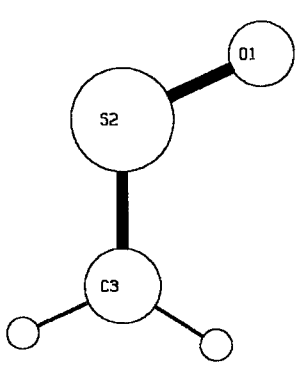
Sulfines (thiocarbonyl S-oxides) are four-centered heterocumulenes with the general formula R1R2C=S=O. The CSO group in sulfines is rigid and nonlinear as indicated by isolation of two stable geometrical isomers[79,80]; E- and Z- of the type R1R2CSO, where R1 ≠ R2. The sulfine carbon atom was revealed to be sp^2 hybridized and the sulfine oxygen atom lies almost in this plane while the CSO angle ranges to 109.0°- 116.0 °[81]. Many experimental tools were used to elucidate the geometrical structure of different sulfines, X-ray[81], microwave[5], photoelectron spectra[6] and NMR[14,23,25].

Theoretically, there has been very little theoretical work on the structure determination of sulfines. Flood and Boggs[82] reported SCF calculation of the structure and bonding of the parent sulfine (R1 = R2 = H). They concluded that the bonding is dative (dipolar), corresponding to the structure $H_2C=S^+—O^-$. Van Lierop et al.[27] reported a series of molecular orbital calculations for sulfine and halogen substituted sulfines using ab initio and INDO methods. They found little effect of substituents on geometry and ground state properties of CSO group of sulfine. Karlstorm et al.[83] reported a complete active space SCF (CASSCF) study of the photo chemistry of H_2CSO, which gave some predictions for the vertical excitation energy to various excited electronic states but did not provide any new information on the ground state.

Ab initio studies of hyper valent sulfur-containing molecules are notoriously difficult and sometimes show large basis set effects[84]. Particularly, Burgers and co-workers found that standard G1 and G2 calculations did not provide an accurate heat of formation because of the inadequate basis set (6-31G(d)) that was used for geometry optimization[1]. Those authors have shown that larger split-valence basis sets e.g. 6-311+G(2df,2p) were required to obtain reliable equilibrium structures. In addition, uncorrelated geometries using large basis sets fail to produce experimental trends.

3.1.1. METHANETHIAL S-OXIDE

It is the simplest molecule of sulfines (parent) where R1 = R2 =H. It is a short lived molecule and was prepared in the gas phase by flash vacuum pyrolysis of 1,3-dithiethane 1-oxide[5], and identified by its microwave[5] and photoelectron spectrum[6].



Owing to its simplicity and low molecular weight, there are many molecular orbital calculations on ; its geometrical structure[27], IR spectra[31], dimerization[38], heat of formation[1,39,85,86] and excited states[30].

In this work, the geometrical structure of the parent sulfine was optimized at different levels of calculations ; RHF, MP2 and B3LYP with various basis sets ranging from valence double zeta (6-31G) to valence triple zeta plus polarization with diffuse functions (6-311+G**) in a systematic attempt to obtain a blanced theoretical description of the sulfine structure. The results are given in table (1), including the experimental results[1] and the other obtained theoretical results in literature[38] for comparison.

Molecular orbital calculations show that the parent sulfine exists in a planar with bent CSO structure and the value of CSO angle is nearly 114.0°. The comparison between these theoretical results obtained at different levels and basis sets 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 (HF/6-31G), the S-C and S-O bond lengths are overestimated with maximum error of 0.217A° and 6.5 ° for CSO angle. With enlarging the basis set to 6-311+G** and inclusion of electron correlation, the experimental results are reproduced with a maximum error of 0.01A° and 0.7°.

Table (1) : Geometrical parameter of the parent sulfine (H_2CSO) calculated at different levels and basis sets.

	Bond lengths (Angstrom)				Bond angles (Degree)			Twist angle (Degree)
	S=O	C=S	C-H_s	C-H_a	CSO	H_sCS	H_aCS	H_s
(RHF)								
6-31G	1.686	1.633	1.072	1.070	108.12	120.37	119.74	0.0
6-311G	1.695	1.623	1.069	1.068	107.12	120.31	119.79	0.0
6-31+G*	1.458	1.584	1.074	1.074	115.18	122.88	116.67	0.0
6-31+G**	1.446	1.581	1.073	1.073	115.28	122.84	116.15	0.0
6-311+G**	1.440	1.579	1.071	1.071	115.36	123.04	115.91	0.0
6-311+G*	1.454	1.584	1.075	1.074	114.59	122.66	116.65	0.0
TZV	1.680	1.631	1.070	1.069	108.17	120.66	119.49	0.0
DZV	1.673	1.628	1.071	1.069	107.46	120.54	119.79	0.0
(MP2)								
6-31G	1.613	1.704	1.086	1.085	112.52	121.00	116.06	0.0
6-311G	1.606	1.693	1.082	1.081	111.34	120.66	116.04	0.0
6-31+G*	1.494	1.626	1.080	1.080	115.34	122.72	115.85	0.0
6-31+G**	1.486	1.626	1.081	1.081	115.54	122.68	115.18	0.0
6-311+G**	1.479	1.621	1.078	1.079	115.43	122.97	114.72	0.0
6-311+G*	1.484	1.625	1.085	1.084	114.64	122.34	115.70	0.0
TZV	1.606	1.697	1.081	1.080	112.29	121.18	115.82	0.0
DZV	1.601	1.708	1.092	1.090	111.36	120.72	116.20	0.0
(B3LYP)								
6-311G**	1.496	1.621	1.083	1.084	114.48	122.91	116.15	0.0
Expermental*	1.469(2)	1.610(2)	1.083(1)	1.077(1)	114.72(2)	122.51(4)	115.63(5)	

(*) From the microwave spectrum. Ref. [8] .

All levels do not show the observed difference in C-H bond length (0.006A°) but give nearly the same bond length for the two bonds.

Arnaud et al.[38] calculated the geometrical parameters of sulfine showing that at the HF level, the disagreement between calculated and experimental geometry increases with increase of the basis set. While the opposite trend was observed when electron correlation is taken into account and the best agreement with experimental results is achieved when one puts f function on heavy atoms. The closest calculated geometry to the experimental one is that calculated at the B3LYP/6-311++G(3df,2p), table (2). On the other hand, Oscar Venture and co-workers[85] used B3LYP to calculate the heat of formation of sulfine. They compared the geometries calculated at the B3LYP, CASSCF, MP2 and CCSD levels; they found that any difference between the methods can not be caused by differences in geometry since all the optimized geometries differ very little. On the other hand, they found that there is no significant multi-configurational component in the ground state of sulfine, since mono-configurational methods like MP2 and CCSD(T) give similar results to CASSCF, or, at least, that any such components that may exist does not affect the equilibrium geometry of the molecule.

Sulfine molecule can be represented by form (**A**) (heterocumulene with a tetravalent sulfur), and can also be alternatively viewed in terms of the charge-separated resonance structures **B** and **C**, known as 1,3-dipoles.

Table (1) : Geometrical parameter of the parent sulfine (H_2CSO) calculated at different levels and basis sets.

	Bond lengths (Angstrom)				Bond angles (Degree)			Twist angle (Degree)
	S=O	C=S	C-H_s	C-H_a	CSO	H_sCS	H_aCS	H_s
(RHF)								
6-31G	1.686	1.633	1.072	1.070	108.12	120.37	119.74	0.0
6-311G	1.695	1.623	1.069	1.068	107.12	120.31	119.79	0.0
6-31+G*	1.458	1.584	1.074	1.074	115.18	122.88	116.67	0.0
6-31+G**	1.446	1.581	1.073	1.073	115.28	122.84	116.15	0.0
6-311+G**	1.440	1.579	1.071	1.071	115.36	123.04	115.91	0.0
6-311+G*	1.454	1.584	1.075	1.074	114.59	122.66	116.65	0.0
TZV	1.680	1.631	1.070	1.069	108.17	120.66	119.49	0.0
DZV	1.673	1.628	1.071	1.069	107.46	120.54	119.79	0.0
(MP2)								
6-31G	1.613	1.704	1.086	1.085	112.52	121.00	116.06	0.0
6-311G	1.606	1.693	1.082	1.081	111.34	120.66	116.04	0.0
6-31+G*	1.494	1.626	1.080	1.080	115.34	122.72	115.85	0.0
6-31+G**	1.486	1.626	1.081	1.081	115.54	122.68	115.18	0.0
6-311+G**	1.479	1.621	1.078	1.079	115.43	122.97	114.72	0.0
6-311+G*	1.484	1.625	1.085	1.084	114.64	122.34	115.70	0.0
TZV	1.606	1.697	1.081	1.080	112.29	121.18	115.82	0.0
DZV	1.601	1.708	1.092	1.090	111.36	120.72	116.20	0.0
(B3LYP)								
6-311G**	1.496	1.621	1.083	1.084	114.48	122.91	116.15	0.0
Expermental*	1.469(2)	1.610(2)	1.083(1)	1.077(1)	114.72(2)	122.51(4)	115.63(5)	

(*) From the microwave spectrum. Ref. [8] .

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Arnaud et al.[38] calculated the geometrical parameters of sulfine showing that at the HF level, the disagreement between calculated and experimental geometry increases with increase of the basis set. While the opposite trend was observed when electron correlation is taken into account and the best agreement with experimental results is achieved when one puts f function on heavy atoms. The closest calculated geometry to the experimental one is that calculated at the B3LYP/6-311++G(3df,2p), table (2). On the other hand, Oscar Venture and co-workers[85] used B3LYP to calculate the heat of formation of sulfine. They compared the geometries calculated at the B3LYP, CASSCF, MP2 and CCSD levels; they found that any difference between the methods can not be caused by differences in geometry since all the optimized geometries differ very little. On the other hand, they found that there is no significant multi-configurational component in the ground state of sulfine, since mono-configurational methods like MP2 and CCSD(T) give similar results to CASSCF, or, at least, that any such components that may exist does not affect the equilibrium geometry of the molecule.

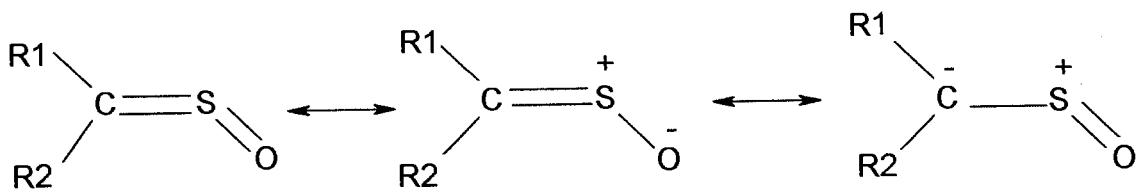
Sulfine molecule can be represented by form (**A**) (heterocumulene with a tetravalent sulfur), and can also be alternatively viewed in terms of the charge-separated resonance structures **B** and **C**, known as 1,3-dipoles.

Table (2) : Geometries and dipole moment (μ) of parent sulfine at various levels of calculation.

Level of calculation	S-O (A°)	S-C (A°)	OSC (deg.)	μ (D)
HF/6-31+G(d,p)[a]	1.462	1.587	114.6	4.03
HF/6-311+G(d,p)	1.456	1.585	114.6	4.09
HF/6-311+G(2df,2p)	1.439	1.579	115.2	3.59
HF/6-311+G(3df,2p)	1.433	1.576	115.5	3.50
B3LYP/6-31+G(d,p)	1.498	1.625	115.1	3.12
B3LYP/6-311+G(2df,2p)	1.479	1.611	114.9	3.19
B3LYP/6-311+G(3df,2p)	1.472	1.607	115.2	3.11
B3LYP/6-31+G(d,p),S(3df)	1.480	1.614	115.0	3.23
MP2/6-31+G(d,p)	1.501	1.630	114.6	4.39
QCISD/6-31+G(d,p)	1.510	1.626	113.2	4.41

[a] These results are taken from Ref. [38] and references there in.

The two formulas **B** and **C** yielding a resonance structures known as 1,3-dipoles.



(A) (B) (C)

The C-S bond length in sulfine is found to be 1.610 A°, which is longer than that of H_2CS (thioformaldehyde), 1.589 A° [43], and is shorter than C-S bond of thioformic acid (HCOSH), 1.806A° [87]. These findings indicate a mainly perturbed double bond character of C-S bond in sulfine. The elongation of C-S bond in sulfine than in thioformaldehyde (C=S), 0.021 A°, represents its contamination by 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 A° [87] and that of pure S=O, 1.500 A° bond.

The characteristic charge separation is reflected in the calculated atomic charges, which is collected in table (3). The sulfur atom possesses a positive charge while both of oxygen and carbon atoms of sulfine group are negatively charged. The above results reveal the preference of the charge separated resonance structures than the nature one.

Table (3) : Total energy , net charges , bond orders and dipole moment of the parent sulfine (H_2CSO) calculated at different levels and basis sets.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C	H_S	H_a	S=O	C=S	C-H_S	C-H_a	
(RHF)											
6-31G	-511.17685	-0.75	0.80	-0.58	0.27	0.24	1.05	1.67	0.90	0.91	5.48
6-311G	-511.23114	-0.71	0.71	-0.52	0.27	0.25	1.01	1.69	0.89	0.89	5.51
6-31+G*	-511.31818	-0.70	0.79	-0.49	0.21	0.18	1.46	1.67	0.94	0.94	3.78
6-31+G**	-511.33502	-0.61	0.61	-0.30	0.16	0.15	1.65	1.77	0.96	0.96	3.47
6-311+G**	-511.39409	-0.69	0.72	-0.14	0.05	0.06	1.64	1.81	0.99	0.98	3.47
6-311+G*	-511.36730	-0.66	0.79	-0.47	0.18	0.16	1.43	1.67	0.95	0.95	3.88
TZV	-511.24540	-0.70	0.72	-0.50	0.26	0.22	0.97	1.73	0.92	0.89	5.73
DZV	-511.19910	-0.76	0.79	-0.56	0.28	0.25	1.02	1.68	0.90	0.89	5.65

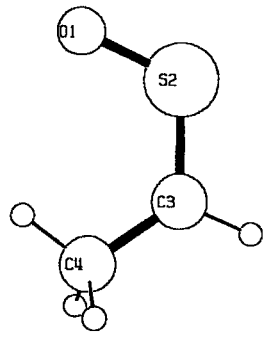
Table (3) continue.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C	H_S	H_a	S=O	C=S	C-H_S	C-H_a	
(MP2)											
6-31G	-511.47658	-0.63	0.85	-0.63	0.22	0.19	1.30	1.27	0.90	0.89	3.54
6-311G	-511.55467	-0.63	0.83	-0.65	0.24	0.22	1.24	1.26	0.88	0.87	3.58
6-31+G*	-511.77919	-0.54	0.68	-0.47	0.18	0.16	1.47	1.40	0.91	0.90	2.84
6-31+G**	-511.83560	-0.46	0.50	-0.31	0.14	0.13	1.66	1.52	0.92	0.91	2.63
6-311+G**	-511.92007	-0.51	0.60	-0.20	0.05	0.07	1.63	1.55	0.94	0.93	2.62
6-311+G*	-511.86294	-0.50	0.69	-0.51	0.17	0.15	1.44	1.39	0.91	0.90	2.77
TZV	-511.57575	-0.61	0.82	-0.65	0.24	0.20	1.19	1.34	0.89	0.86	3.86
DZV	-511.49893	-0.66	0.86	-0.67	0.25	0.22	1.23	1.28	0.88	0.86	3.65
(B3LYP)											
6-311G**	-512.71885	-0.44	0.51	-0.43	0.22	0.14					3.48
Expermental*											2.99

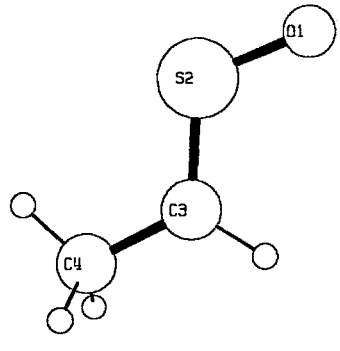
(*) From the microwave spectrum. Ref. [8].

3.1.2. ETHANETHIAL S-OXIDE

Alkyl sulfines are unstable compounds. Propanethial S-oxide is of particular inters to Allium chemistry where there is substantial evidence that it is the onion lachrymatory factor[38]. Microwave studies have identified Z-ethanethial S-oxide[80,6], 3-fold methyl internal rotation barrier of 0.400 kcal/mol was calculated, the early theoretical value is 0.8 kcal/mol[5], while the Z/E ratio is found as 97/3. Recently, J. Z. Gillies[88] investigated the microwave process of Z- and E-ethanethial S-oxide, the internal structure was elucidated, internal rotational barrier and the electronic dipole moment were investigated.



Z-form



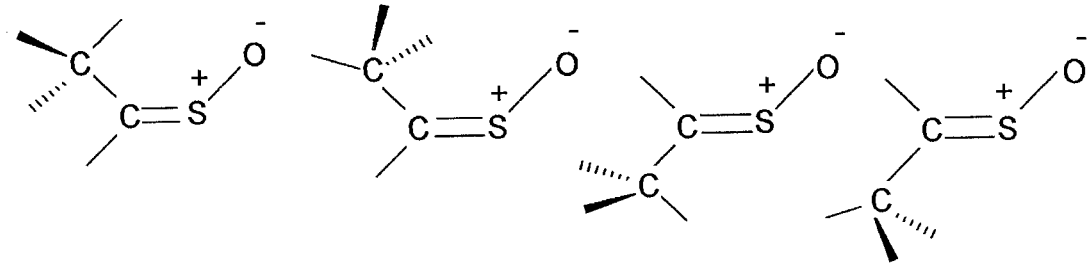
E-form

A number of alkyl and aryl substituted sulfines were isolated and characterized by spectroscopic methods or X-ray crystalography[4,89]. The most famous alkyl sulfine is propanethial S-oxide which is the lachrymatory factor of onion[13]. The experimentally prepared ethanethial S-oxide is proved to be, using ^{1}HNMR and microwave spectroscopy, in Z-form and the presence of E-form does not exceed 5%[90].

E. Block et al.[28] studied experimentally and theoretically, using RHF level of calculation, the conformational preference of CH_3CHSO molecule.

In this work, this methyl derivative is fully optimized at both its stereoisomers at the same levels of work. The calculations show that the Z- and E-isomers of ethanethial S-oxide have nearly the same geometrical parameters except for $S_2C_3C_4$ angle, where it is greater by $\approx 5^\circ$ for the Z-isomer. The methyl group has no effect on the geometry of sulfine group or its charge distribution, tables (4,5). The molecular orbital calculations at various levels and basis sets show that the Z-form is less in energy than the corresponding E-isomer.

Ethanethial S-oxide can exist in the following conformers through the rotation around C_3-S_2 bond or free rotation of CH_3 group around C_3-C_4 bond.

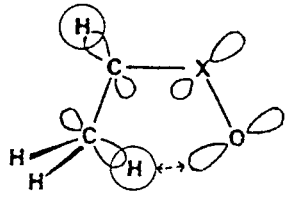


(A) **(B)** **(C)** **(D)**

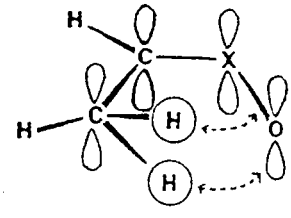
The conformers (**A**) and (**B**) are Z forms, where conformer (**A**) is found to be more stable than the corresponding (**B**) form by 1.12 kcal/mol at MP2 level. On the other hand, the energy of E-forms (**C** and **D**) are 2.66

and 5.38 kcal/mol higher in energy than conformer **A**, at the MP2 level of calculation. A previous work[28] showed also that conformer **A** is 0.8 kcal/mol less than **B** at RHF while **C** and **D** are 1.7 and 3.1 kcal/mol more in energy. The difference in stability between the four forms is attributed to electrostatic interaction between positively methyl hydrogen atom (charge = 0.07) and the negative terminal oxygen atom (charge = -0.53) where the distance calculated between these two atoms is 2.63, 2.56 and 2.57 A° at the HF/6-311+G**, MP2/6-311+G** and B3LYP/6-311G** levels, respectively. This interaction is negligible in the E-forms (**C**,**D**).

Another important reason for the stabilization of Z-form over the E-one is the orbital-orbital interactions. The π-type of orbital interaction is due to the formation of aromatic 6-π electron system and this type favor form (**B**) over the E-form. The other orbital interaction type which stabilizes the (**A**) form is the formation of 6σ-MOs of which is the HOMO is bonding.



σ-stabilization



π-stabilization

Table (4) : Geometrical parameters of the two isomers of sulfine (CH_3CHSO) calculated at different levels and basis sets.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C_3=O	C_3-C_4	C_3-H_8	O-H_6	CSO	C_4C_3S	H_8CS	
(RHF) 6-31G	1.702 (1.707)	1.651 (1.647)	1.482 (1.485)	1.074 (1.075)	2.432	107.06 (106.58)	124.83 (124.85)	115.78 (116.05)	0.0 (180.0)
6-311G	1.709 (1.717)	1.640 (1.636)	1.480 (1.484)	1.072 (1.072)	2.430	106.65 (105.58)	125.39 (125.23)	115.39 (115.74)	0.0 (180.0)
6-31+G*	1.466 (1.465)	1.592 (1.592)	1.495 (1.500)	1.077 (1.077)	2.615	114.44 (114.55)	126.52 (122.03)	113.31 (118.34)	0.0 (180.0)
6-31+G**	1.454 (1.453)	1.588 (1.588)	1.495 (1.499)	1.076 (1.076)	2.626	114.77 (114.80)	126.76 (121.35)	112.73 (118.45)	0.0 (180.0)
6-311+G**	1.448 (1.447)	1.587 (1.587)	1.492 (1.496)	1.074 (1.074)	2.625	114.87 (114.90)	126.76 (121.31)	112.63 (118.52)	0.0 (180.0)
6-311+G*	1.463 (1.462)	1.591 (1.591)	1.495 (1.500)	1.078 (1.078)	2.592	113.93 (114.02)	126.36 (122.10)	113.18 (118.06)	0.0 (180.0)
TZV	1.694 (1.702)	1.648 (1.644)	1.480 (1.484)	1.073 (1.074)	2.479	107.37 (106.77)	125.78 (124.66)	115.14 (116.34)	0.0 (180.0)
DZV	1.688 (1.698)	1.644 (1.640)	1.492 (1.496)	1.073 (1.074)	2.443	106.85 (106.07)	125.15 (124.69)	115.95 (116.72)	0.0 (180.0)

Values in parenthesis refer to E-form.

Table (4) continue.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C_3=O	C_3-C_4	C_3-H_8	O-H_6	CSO	C_4C_3S	H_8CS	
(MP2)									
6-31G	1.627 (1.621)	1.704 (1.702)	1.500 (1.508)	1.089 (1.090)	2.520	110.94 (112.06)	123.34 (121.07)	113.41 (116.82)	0.0 (180.0)
6-311G	1.622 (1.617)	1.693 (1.690)	1.496 (1.504)	1.085 (1.086)	2.496	110.26 (110.76)	123.74 (121.62)	112.98 (116.20)	0.0 (180.0)
6-31+G*	1.498 (1.496)	1.633 (1.633)	1.490 (1.497)	1.084 (1.084)	2.559	114.19 (115.28)	124.48 (120.09)	113.28 (118.66)	0.0 (180.0)
6-31+G**	1.491 (1.488)	1.632 (1.632)	1.493 (1.499)	1.085 (1.084)	2.567	114.36 (115.62)	124.53 (119.25)	112.72 (118.82)	0.0 (180.0)
6-311+G**	1.484 (1.481)	1.628 (1.628)	1.488 (1.495)	1.082 (1.082)	2.556	114.33 (115.57)	124.47 (119.18)	112.68 (119.03)	0.0 (180.0)
6-311+G*	1.488 (1.486)	1.632 (1.631)	1.493 (1.500)	1.088 (1.088)	2.536	113.78 (114.77)	124.23 (119.92)	113.07 (118.39)	0.0 (180.0)
TZV	1.622 (1.618)	1.696 (1.693)	1.493 (1.502)	1.084 (1.085)	2.569	111.06 (112.04)	124.56 (120.95)	112.58 (116.99)	0.0 (180.0)
DZV	1.614 (1.611)	1.706 (1.705)	1.519 (1.527)	1.094 (1.097)	2.515	110.17 (111.17)	123.21 (121.02)	113.89 (117.46)	0.0 (180.0)
(B3LYP) 6-311G**	1.500 (1.498)	1.630 (1.630)	1.488 (1.495)	1.086 (1.086)	2.568	113.50 (114.30)	125.07 (121.17)	113.24 (118.11)	0.0 (180.0)
ab initio[a]	1.466	1.593	1.496	1.077		114.4	126.5	113.4	
experimental[b]	1.477(4)	1.618(3)	1.493(3)			113.9(2)	125.4(2)		

Values in parenthesis refer to E-form.

[a] From ref. [91]. [b] From microwave spectra. Ref. [88].

Table (5) : Total energy, net charges, bond orders and dipole moment of the two isomers of sulfine (CH_3CHSO) calculated at different levels and basis sets.

	T.E (Hartree)	Charges					Bond orders					Dipole moment (Debye)
		O	S	C_3	C_4	H_8	S=O	C_3=O	C_3-C_4	C_3-H_8	O-H_6	
(RHF)												
6-31G	-550.21169 (-550.20800)	-0.76 (-0.75)	0.76 (0.75)	-0.41 (-0.40)	-0.51 (-0.51)	0.25 (0.28)	1.02 (1.01)	1.62 (1.64)	0.91 (0.91)	0.91 (0.89)		5.91 (6.63)
6-311G	-550.27269 (-550.26894)	-0.72 (-0.71)	0.66 (0.65)	-0.34 (-0.34)	-0.54 (-0.54)	0.24 (0.27)	0.99 (0.97)	1.66 (1.67)	0.85 (0.84)	0.89 (0.88)		5.95 (6.65)
6-31+G*	-550.36532 (-550.36154)	-0.72 (-0.72)	0.76 (0.75)	-0.34 (-0.33)	-0.36 (-0.37)	0.19 (0.21)	1.42 (1.42)	1.65 (1.66)	0.96 (0.96)	0.94 (0.94)		4.15 (4.62)
6-31+G**	-550.38316 (-550.37987)	-0.64 (-0.65)	0.56 (0.57)	-0.13 (-0.11)	-0.33 (-0.32)	0.14 (0.15)	1.60 (1.62)	1.74 (1.74)	1.01 (1.02)	0.96 (0.95)		3.84 (4.25)
6-311+G**	-550.44915 (-550.44553)	-0.72 (-0.71)	0.70 (0.70)	-0.15 (-0.11)	-0.08 (-0.06)	0.06 (0.03)	1.60 (1.61)	1.79 (1.80)	1.01 (1.02)	0.99 (1.00)		3.88 (4.31)
6-311+G*	-550.42128 (-550.41669)	-0.69 (-0.68)	0.76 (0.76)	-0.41 (-0.39)	-0.22 (-0.22)	0.16 (0.18)	1.39 (1.39)	1.66 (1.66)	0.94 (0.95)	0.94 (0.95)		4.25 (4.75)
TZV	-550.28876 (-550.28551)	-0.71 (-0.69)	0.65 (0.64)	-0.33 (-0.31)	-0.50 (-0.50)	0.23 (0.27)	0.95 (0.94)	1.68 (1.70)	0.96 (0.96)	0.87 (0.89)		6.19 (6.95)
DZV	-550.23705 (-550.23320)	-0.78 (-0.76)	0.72 (0.69)	-0.35 (-0.33)	-0.51 (-0.51)	0.24 (0.28)	1.01 (0.99)	1.64 (1.63)	0.85 (0.86)	0.90 (0.90)		6.03 (6.82)
Experimental[b]												2.714(5)

Values in parenthesis refer to E-form.

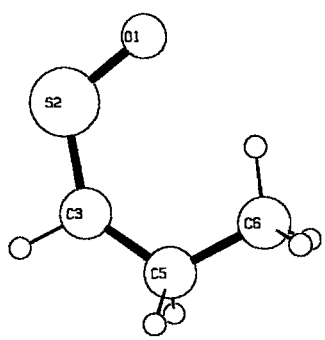
[b] From microwave spectra. Ref. [88].

Table (5) continue.

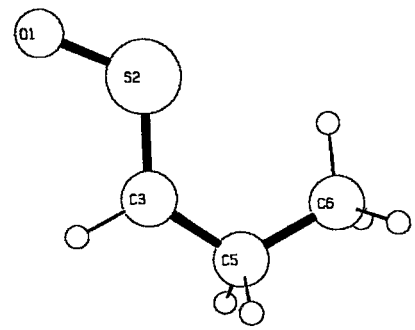
	T.E (Hartree)	Charges					Bond orders					Dipole moment (Debye)
		O	S	C_3	C_4	H_8	S=O	C_3=O	C_3-C_4	C_3-H_8	O-H_6	
(MP2)												
6-31G	-550.59661 (-550.59222)	-0.67 (-0.67)	0.85 (0.85)	-0.48 (-0.47)	-0.43 (-0.43)	0.20 (0.22)	1.24 (1.26)	1.32 (1.31)	0.90 (0.89)	0.89 (0.89)		3.95 (4.46)
6-311G	-550.68791 (-550.68307)	-0.66 (-0.66)	0.82 (0.83)	-0.49 (-0.48)	-0.51 (-0.51)	0.22 (0.24)	1.19 (1.19)	1.33 (1.32)	0.84 (0.83)	0.84 (0.87)	0.06	4.00 (4.52)
6-31+G*	-550.97001 (-550.96621)	-0.56 (-0.56)	0.67 (0.66)	-0.34 (-0.33)	-0.36 (-0.36)	0.16 (0.17)	1.43 (1.45)	1.39 (1.39)	0.94 (0.93)	0.90 (0.90)		3.05 (3.44)
6-31+G**	-551.03758 (-551.03386)	-0.49 (-0.49)	0.48 (0.48)	-0.14 (-0.12)	-0.36 (-0.35)	0.12 (0.12)	1.62 (1.65)	1.49 (1.48)	0.98 (0.98)	0.91 (0.91)		2.87 (3.23)
6-311+G**	-551.13489 (-551.13065)	-0.53 (-0.53)	0.59 (0.59)	-0.19 (-0.15)	-0.17 (-0.15)	0.06 (0.04)	1.60 (1.62)	1.52 (1.53)	0.97 (0.98)	0.93 (0.94)		2.87 (3.25)
6-311+G*	-551.06806 (-551.06356)	-0.52 (-0.51)	0.68 (0.68)	-0.44 (-0.42)	-0.28 (-0.29)	0.15 (0.16)	1.42 (1.42)	1.39 (1.39)	0.91 (0.91)	0.90 (0.91)		2.97 (3.36)
TZV	-550.71139 (-550.70694)	-0.64 (-0.64)	0.80 (0.80)	-0.49 (-0.48)	-0.48 (-0.49)	0.22 (0.26)	1.14 (1.14)	1.39 (1.40)	0.89 (0.91)	0.83 (0.85)		4.29 (4.92)
DZV	-550.61699 (-550.61183)	-0.70 (-0.70)	0.84 (0.83)	-0.46 (-0.45)	-0.51 (-0.50)	0.22 (0.25)	1.18 (1.19)	1.33 (1.32)	0.83 (0.84)	0.86 (0.88)		4.02 (4.64)
(B3LYP)												
6-311G**	-552.04615 (-552.04169)	-0.54 (-0.53)	0.62 (0.62)	-0.39 (-0.37)	-0.27 (-0.28)	0.15 (0.16)						3.59 (4.05)

Values in parenthesis refer to E-form.

The introduction of the electron donating methyl group in sulfine molecule increases and accumulates the charges on sulfur and oxygen atoms while the negative charge on carbon atom decreases to -0.39. This means that the SCO group become less polarized upon substitution. The total bond order of the bonds S=O and C=S decreases upon substitution of CH_3 group in ethanethail S-oxide, tables (3,5) increasing their single bond character. The total bond order of C-C bond is calculated as 1.01 and 0.97 for Z-form and 1.02 and 0.98 for E-form.



Z-form



E-form

Table (6) shows the ground state properties of E- and Z-propanethial S-oxide calculated using 6-31+G* basis set. It is interesting to note that geometry of CSO group does not change when R group is ethyl, except for SCC angle which increases in this case more than for R = Me while the C_3-C_4 bond length elongates by $\approx$ 0.01 A° . The same findings were observed for the charges accumulated on different atoms for both compounds. The Z-isomer is calculated to be 1.63 kcal/mol less than E-form at MP2 level while this value was 2.38 in case of R = Me.

Table (6) : Geometrical parameters of the two isomers of the sulfine (C_2H_5CHSO) calculated at 6-31+G*/RHF and MP2 levels.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angle (Degree)
	S=O	C=S	C_3-C_5	C_3-H_4	O-H_9	CSO	SC_3C_5	SC_3C_4	
(RHF)									
6-31+G*	1.466 (1.468)	1.594 (1.594)	1.503 (1.505)	1.080 (1.078)	2.291	117.63 (113.54)	135.41 (126.89)	108.87 (115.96)	0.0 (180.0)
(MP2)									
6-31+G*	1.498 (1.498)	1.634 (1.635)	1.498 (1.502)	1.088 (1.086)	2.249	118.43 (114.00)	134.75 (125.43)	107.62 (115.73)	0.0 (180.0)

Values in parenthesis refer to E-form.

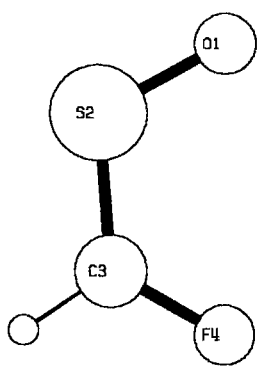
Table (7) : Total energy, net charges, bond orders and dipole moment of the two isomers of the sulfine (C_2H_5CHSO) calculated at 6-31+G*/RHF and MP2 levels.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	H_4	C_5	S=O	C=S	C_3-H_4	C_3-C_5	
(RHF)											
6-31+G*	-589.39341 (-589.39125)	-0.73 (-0.73)	0.75 (0.75)	-0.33 (-0.34)	0.18 (0.21)	-0.23 (-0.24)	1.41 (1.40)	1.65 (1.66)	0.94 (0.94)	0.95 (0.95)	4.20 (4.91)
(MP2)											
6-31+G*	-590.14242 (-590.13982)	-0.56 (-0.57)	0.66 (0.67)	-0.34 (-0.35)	0.15 (0.17)	-0.22 (-0.22)	1.43 (1.43)	1.39 (1.39)	0.89 (0.90)	0.92 (0.92)	3.14 (3.72)

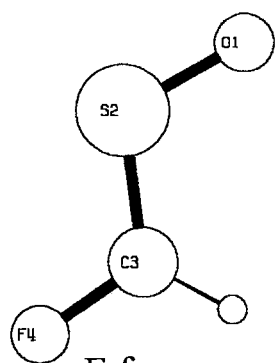
Values in parenthesis refer to E-form.

3.1.3. FLUORINE SUBSTITUTED SULFINE

Replacing one hydrogen of the parent sulfine by a flouro atom results in two different geometrical isomers corresponding to E- and Z-stereoisomers of fluorine substituted sulfine, as shown below. It was observed that the parent sulfine H_2CSO and halogen-substituted sulfines HXCSO are fairly unstable[1,92]. J. Lierop and A. Avoird[27] studied theoretically, using ab initio and INDO method, the geometries and electronic structures of chloro and flouro sulfines.



Z-form



E-form

In our work, the two isomers are optimized at different levels and various basis sets as in the case of the parent sulfine, and the results are represented in tables (8,9). The Z-form is calculated to be more stable than the E-form, the maximum difference is about 2 kcal/mol. The difference in energy increases with the addition of polarized functions and electron correlation. The two isomers are coplanar and their bond lengths and bond angles depend on the type of the isomer.

As shown in table (8), the S-O, C-S and C-F bond lengths are more longer in E-form than the Z-form while the angles OSC and SCF is less

by about 3 ° and 6 °, respectively. On the other hand, the existence of fluorine atom does not appreciably alter the geometry of the sulfine molecule; the most affected bond is the C-S bond which elongates by about 0.01 A°.

The above results are reflected on the values of the total bond order of the various bonds on flouro derivative. The total bond order of the two bonds, S-O and S-C, in case of the Z-form is greater than that in the E-one by about 0.03. The comparison between table (3) and (9) shows that the total bond orders of the parent sulfine bonds is greater, indicating less double bond character of CSO group bonds.

Table (9) shows the Mulliken atomic charges of fluorine substituted sulfine. It is noted that the atomic charges on the different atoms of the Z-form is less than that of the E-form. The atomic charge on both oxygen and sulfur atoms in the two isomers does not appreciably affected by the fluoride substitution on the carbon comparing to the carbon atom reduction. The fluorine atom possesses a negative charge which is completely compensated by the carbon atom. The charge on the carbon atom changes from negative value in parent sulfine to nearly zero charge or positive one in flouro derivative owing to the high electronegative fluorine atom. Thus the fluorine substitution decreases the polarization of C-S bond. and therefore the same results were obtained by both Bernardi et al.[93] and Lierop and Avoird[27] at low level of calculations.

Table (8) : Geometrical parameters of the two isomers of sulfine (HFCSO) calculated at different levels and basis sets.

	Bond lengths (Angstrom)				Bond angles (Degree)			Twist angles (Degree)
	S=O	C=S	C-F	C-H	CSO	FCS	HCS	
(RHF)								
6-31G	1.721 (1.736)	1.638 (1.638)	1.334 (1.339)	1.069 (1.070)	108.69 (102.38)	123.71 (121.24)	122.54 (123.83)	0.0 (180.0)
6-311G	1.734 (1.754)	1.626 (1.626)	1.330 (1.338)	1.067 (1.067)	107.82 (101.68)	124.29 (121.65)	122.36 (123.96)	0.0 (180.0)
6-31+G*	1.463 (1.469)	1.596 (1.599)	1.303 (1.312)	1.074 (1.074)	114.73 (111.51)	124.82 (119.14)	119.43 (124.90)	0.0 (180.0)
6-31+G**	1.450 (1.457)	1.593 (1.596)	1.297 (1.306)	1.073 (1.072)	114.94 (111.79)	125.49 (119.84)	118.31 (124.03)	0.0 (180.0)
6-311+G**	1.444 (1.450)	1.592 (1.595)	1.296 (1.306)	1.072 (1.071)	115.19 (111.99)	125.72 (119.73)	118.21 (124.25)	0.0 (180.0)
6-311+G*	1.459 (1.466)	1.595 (1.598)	1.299 (1.309)	1.075 (1.074)	114.26 (111.02)	124.96 (119.48)	119.15 (124.58)	0.0 (180.0)
TZV	1.711 (1.737)	1.637 (1.636)	1.324 (1.331)	1.068 (1.068)	108.80 (102.84)	124.33 (121.57)	122.10 (124.28)	0.0 (180.0)
DZV	1.707 (1.732)	1.631 (1.630)	1.337 (1.346)	1.069 (1.070)	108.64 (102.55)	124.49 (121.77)	122.02 (123.87)	0.0 (180.0)

Values in parenthesis refer to E-form.

Table (8) continue.

	Bond lengths (Angstrom)				Bond angles (Degree)			Twist angles (Degree)
	S=O	C=S	C-F	C-H	CSO	FCS	HCS	
(MP2)								
6-31G	1.616 (1.624)	1.708 (1.707)	1.395 (1.401)	1.084 (1.085)	112.66 (108.97)	121.86 (116.51)	120.87 (125.80)	0.0 (180.0)
6-311G	1.609 (1.619)	1.696 (1.695)	1.395 (1.405)	1.080 (1.080)	111.75 (107.79)	122.37 (117.21)	120.88 (125.83)	0.0 (180.0)
6-31+G*	1.496 (1.499)	1.640 (1.643)	1.339 (1.348)	1.082 (1.082)	114.73 (122.18)	123.60 (117.68)	119.63 (125.49)	0.0 (180.0)
6-31+G**	1.489 (1.492)	1.639 (1.644)	1.328 (1.338)	1.083 (1.082)	114.97 (112.23)	124.48 (118.73)	118.43 (124.33)	0.0 (180.0)
6-311+G**	1.481 (1.484)	1.637 (1.642)	1.328 (1.338)	1.081 (1.080)	115.20 (112.12)	124.95 (118.65)	118.20 (124.70)	0.0 (180.0)
6-311+G*	1.486 (1.489)	1.640 (1.643)	1.330 (1.341)	1.086 (1.086)	114.28 (111.47)	123.92 (118.47)	119.26 (124.80)	0.0 (180.0)
TZV	1.607 (1.617)	1.703 (1.702)	1.389 (1.401)	1.078 (1.078)	112.81 (108.99)	122.53 (117.07)	120.87 (126.58)	0.0 (180.0)
DZV	1.601 (1.609)	1.712 (1.712)	1.409 (1.422)	1.088 (1.090)	112.38 (108.36)	122.36 (117.00)	121.18 (126.51)	0.0 (180.0)
(B3LYP)								
6-311G**	1.497 (1.501)	1.639 (1.642)	1.325 (1.335)	1.086 (1.085)	114.32 (111.35)	124.31 (118.80)	119.42 (124.94)	0.0 (180.0)

Values in parenthesis refer to E-form.

Table (9): Total energy, net charges, bond orders and dipole moment of the two isomers of sulfine (HFCSO) calculated at different levels and basis sets.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C	F	H	S=O	C=O	C-F	C-H	
(RHF)											
6-31G	-609.98050 (-609.98536)	-0.68 (-0.70)	0.74 (0.74)	0.02 (0.02)	-0.33 (-0.35)	0.26 (0.29)	1.00 (0.96)	1.59 (1.61)	0.82 (0.79)	0.88 (0.87)	5.94 (3.50)
6-311G	-610.06759 (-610.07219)	-0.64 (-0.65)	0.62 (0.63)	0.07 (0.06)	-0.30 (-0.32)	0.25 (0.28)	0.96 (0.92)	1.61 (1.66)	0.84 (0.80)	0.87 (0.86)	5.93 (3.49)
6-31+G*	-610.14899 (-610.14914)	-0.70 (-0.72)	0.73 (0.74)	0.09 (0.09)	-0.30 (-0.31)	0.18 (0.21)	1.44 (1.40)	1.61 (1.62)	0.92 (0.89)	0.93 (0.92)	4.39 (2.71)
6-31+G**	-610.16946 (-610.16751)	-0.62 (-0.64)	0.54 (0.55)	0.19 (0.21)	-0.26 (-0.28)	0.15 (0.16)	1.64 (1.60)	1.70 (1.71)	1.05 (1.01)	0.95 (0.94)	3.91 (2.46)
6-311+G**	-610.26001 (-610.25762)	-0.69 (-0.70)	0.66 (0.67)	0.29 (0.30)	-0.30 (-0.31)	0.04 (0.04)	1.63 (1.60)	1.78 (1.78)	0.97 (0.93)	1.00 (1.01)	3.96 (2.41)
6-311+G*	-610.22762 (-610.22693)	-0.66 (-0.68)	0.72 (0.74)	-0.004 (-0.01)	-0.21 (-0.22)	0.15 (0.17)	1.41 (1.36)	1.62 (1.64)	0.98 (0.94)	0.94 (0.94)	4.54 (2.75)
TZV	-610.09524 (-610.09781)	-0.64 (-0.65)	0.63 (0.65)	0.01 (-0.01)	-0.23 (-0.24)	0.23 (0.26)	0.95 (0.89)	1.63 (1.73)	0.88 (0.86)	0.88 (0.87)	6.07 (3.73)
DZV	-610.03151 (-610.03437)	-0.69 (-0.70)	0.71 (0.71)	-0.05 (-005)	-0.23 (-0.26)	0.26 (0.30)	099 (0.96)	1.59 (1.65)	0.92 (0.90)	0.87 (0.86)	6.06 (3.60)

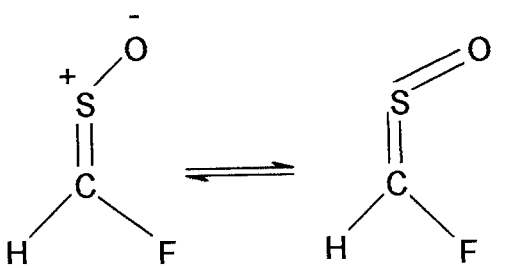
Values in parenthesis refer to E-form.

Table (9) continue.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C	F	H	S=O	C=O	C-F	C-H	
(MP2)											
6-31G	-610.40015 (-610.40176)	-063 (-0.65)	0.85 (0.86)	-0.13 (-0.14)	-0.29 (-0.30)	0.20 (0.23)	1.27 (1.24)	1.21 (1.25)	0.79 (0.77)	0.86 (0.86)	4.47 (2.01)
6-311G	-610.52411 (-610.52533)	-0.63 (-0.65)	0.80 (0.82)	-0.11 (-0.12)	-0.28 (-0.30)	0.22 (0.24)	1.22 (1.18)	1.21 (1.26)	0.80 (0.76)	0.84 (0.84)	4.55 (2.02)
6-31+G*	-610.77318 (-610.77251)	-0.55 (-0.56)	0.64 (0.62)	0.003 (-0.004)	-025 (-0.26)	0.15 (0.17)	1.45 (1.42)	1.34 (1.34)	0.91 (0.88)	0.88 (0.89)	3.41 (1.79)
6-31+G**	-610.86409 (-610.86148)	-0.47 (-0.48)	0.45 (0.47)	0.09 (0.09)	-0.19 (-0.21)	0.13 (0.14)	1.64 (1.62)	1.44 (1.44)	1.06 (1.02)	0.90 (0.90)	3.07 (1.71)
6-311+G**	-611.00439 (-611.00154)	-0.52 (-0.53)	0.54 (0.56)	0.18 (0.19)	-0.24 (-0.25)	0.04 (0.04)	1.62 (1.59)	1.51 (1.50)	0.96 (0.93)	0.93 (0.95)	3.13 (1.64)
6-311+G*	-610.92451 (-610.92296)	-0.51 (-0.52)	0.63 (0.66)	-0.09 (-0.11)	-0.17 (-0.19)	0.13 (0.15)	1.42 (1.39)	1.34 (1.35)	0.96 (0.92)	0.89 (0.90)	3.46 (1.73)
TZV	-610.56335 (-610.56197)	-0.60 (-0.63)	0.78 (0.82)	-0.18 (-0.19)	-0.21 (-0.23)	0.20 (0.23)	1.19 (1.14)	1.27 (1.36)	0.83 (0.81)	0.83 (0.84)	4.70 (2.16)
DZV	-610.44441 (-610.44347)	-0.65 (-0.68)	0.85 (0.86)	-0.19 (-0.19)	-0.22 (-0.24)	0.22 (0.25)	1.21 (1.19)	1.21 (1.26)	0.89 (0.86)	0.83 (0.84)	4.64 (1.86)
(B3LYP)											
6-311+G**	-611.95904 (-611.95824)	-0.52 (-0.53)	0.59 (0.62)	-0.07 (-0.08)	-0.15 (-0.17)	015 (0.16)					3.79 (2.21)
Lierop et al*		-0.67 (-0.69)	0.61 (0.63)	0.14 (0.14)	-0.36 (-0.38)	0.28 (0.30)					5.26 (2.493)

Values in parenthesis refer to E-form. (*) see ref. [27].

The electron distribution in flourosulfine explains the slight difference in geometrical and stability than the parent sulfine.



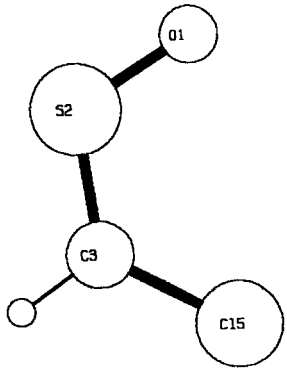
(A) (B)

Flourosulfine molecule can exist only in either native structure (**A**) or structure (**B**), while the second dipolar structure in parent sulfine is not favored. The form (**A**) is expected to be the predominant. Since the charges on both oxygen and sulfur atoms are almost constant in flouro substituted and non substituted sulfine, it is nature and lengths are also the same in both compounds.

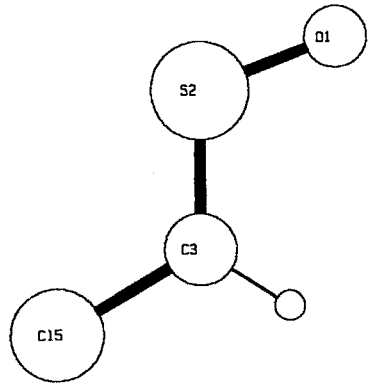
3.1.4. CHLUORINE SUBSTITUTED SULFINE

The chloro-substituted sulfine was studied at 6-311+G** basis sets using the different levels. The chlourine atom has low value of electronegativity relative to that of flourine atom which is reflected on the properties sulfines, especially the net charges.

Energetically, the E-form of chloro sulfine is more stable than E-form by 360.36 au. The Z-form of chloro sulfine is more stable than Z-form of flouro sulfine by 360.37 au.



Z-form



E-form

Table (11) shows the Mulliken atomic charges on different centers of E- and Z-chloro sulfine calculated at the three levels. The effect of low electronegativity of chlouro atom compared to that of flouro is so clear on the charge on carbon atom. The charge value is high negative (-0.05, -0.11, -0.41) at the three levels in case of chlouro. The same trend is found for the charge on sulfur atom which becomes more positive, while the charge on oxygen atom becomes less negative. This means that the sulfinic group is more polarized in case of chlouro atom and this facilitates the carbophilic reaction.

Table (10): Geometrical parameters of the two isomers of sulfine (ClCHSO) calculated at 6-311+G**/RHF, MP2 and B3LYP.

	Bond lengths (Angstrom)				Bond angles (Degree)			Twist angle (Degree)
	S=O	C=S	C-Cl	C-H	CSO	ClCS	HCS	
(RHF)								
6-311+G**	1.438 (1.442)	1.589 (1.590)	1.707 (1.720)	1.070 (1.070)	115.57 (113.03)	126.06 (120.33)	116.44 (122.55)	0.0 (180.0)
(MP2)								
6-311+G**	1.479 (1.481)	1.639 (1.642)	1.712 (1.728)	1.079 (1.079)	114.61 (112.96)	124.17 (119.04)	116.76 (122.57)	0.0 (180.0)
(B3LYP)								
6-311G**	1.491 (1.496)	1.638 (1.640)	1.712 (1.727)	1.083 (1.083)	114.51 (111.91)	125.59 (121.11)	116.97 (121.98)	0.0 (180.0)

Values in parenthesis refer to E-form.

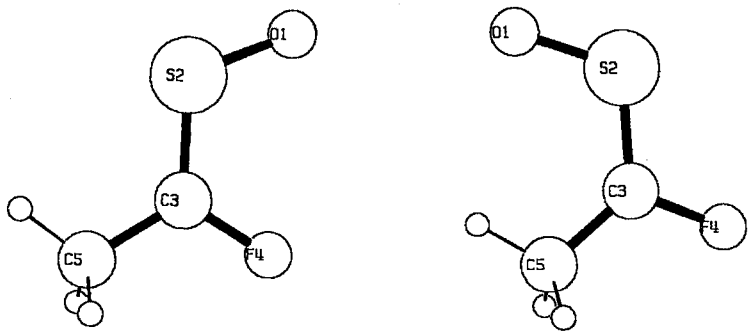
Table (11) : Total energy, net charges, bond orders and dipole moment of the two isomers of sulfine (ClCHSO) calculated at 6-311+G**/RHF, MP2 and B3LYP.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C	Cl	H	S=O	C=S	C-Cl	H	
(RHF)											
6-311+G**	-970.31433 (-970.31095)	-0.68 (-0.69)	0.71 (0.73)	-0.05 (-0.01)	-0.05 (-0.07)	0.06 (0.05)	1.66 (1.63)	1.75 (1.78)	1.11 (1.07)	1.00 (1.01)	3.50 (2.29)
(MP2)											
6-311+G**	-970.99457 (-970.99018)	-0.50 (-0.51)	0.57 (0.59)	-0.11 (-0.09)	-0.03 (-0.05)	0.07 (0.05)	1.63 (1.61)	1.46 (1.48)	1.06 (1.02)	0.94 (0.95)	2.76 (1.54)
(B3LYP)											
6-311G**	-972.32936 (-972.32517)	-0.50 (-0.51)	0.67 (0.69)	-0.41 (-0.41)	0.04 (0.02)	0.20 (0.21)					3.34 (2.14)
Lierpo et al.(*)		-0.69 (-0.70)	0.64 (0.65)	-0.37 (0.36)	0.13 (0.09)	0.29 (0.31)					4.52 (3.87)

Values in parenthesis refer to E-form.

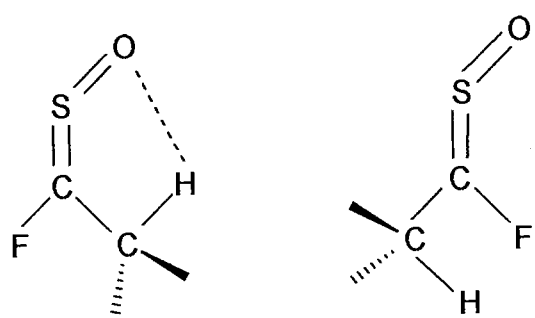
(*) see ref. [27].

3.1.5. FLOURO METHYL SULFINE



Z-form E-form

To examine the main affecting factor on the geometry and stability of both isomers, the titled compound was examined. This molecule contains, flour atom which has the maximum electronegative value and the methyl group that can exhibit an electrostatic attraction with the terminal oxygen atom. The two forms of such molecule are the E-form containing the electrostatic attraction while in the Z-form the methyl group is directed away from the oxygen atom.



E form Z form

(electrostatic attraction)

Table (12) : Geometrical parameters of the two isomers of sulfine (FCH_3CSO) calculated at different levels and basis sets.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C=O	C_3-F	C_3-C_4	O-H_7	CSO	FC_3S	C_4C_3S	
(RHF)									
6-31G	1.738 (1.730)	1.659 (1.656)	1.349 (1.3412)	1.471 (1.478)	2.410	102.79 (108.06)	116.99 (120.23)	128.20 (126.64)	180.0 (0.0)
6-311G	1.750 (1.741)	1.646 (1.643)	1.351 (1.340)	1.468 (1.476)	2.417	102.69 (107.39)	116.95 (120.62)	128.82 (126.63)	180.0 (0.0)
6-31+G*	1.478 (1.469)	1.609 (1.606)	1.319 (1.309)	1.482 (1.488)	2.588	111.13 (113.80)	116.11 (121.13)	128.36 (124.25)	180.0 (0.0)
6-31+G**	1.465 (1.456)	1.606 (1.602)	1.313 (1.302)	1.482 (1.488)	2.587	111.77 (114.15)	116.37 (121.71)	127.97 (123.13)	180.0 (0.0)
6-311+G**	1.460 (1.449)	1.605 (1.602)	1.312 (1.302)	1.480 (1.485)	2.580	111.76 (114.38)	116.47 (121.79)	127.86 (123.09)	180.0 (0.0)
6-311+G*	1.475 (1.466)	1.607 (1.605)	1.316 (1.305)	1.481 (1.488)	2.555	110.75 (113.50)	116.38 (121.32)	127.86 (123.78)	180.0 (0.0)
TZV	1.734 (1.721)	1.657 (1.654)	1.342 (1.331)	1.469 (1.477)	2.445	103.37 (108.31)	116.91 (120.63)	128.65 (125.94)	180.0 (0.0)
DZV	1.730 (1.721)	1.651 (1.648)	1.357 (1.346)	1.482 (1.490)	2.425	103.29 (108.14)	117.40 (120.92)	128.12 (126.10)	180.0 (0.0)

Values in parenthesis refer to Z-form.

Table (12) continue.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C=O	C_3-F	C_3-C_4	O-H_7	CSO	FC_3S	C_4C_3S	
(MP2)									
6-31G	1.642 (1.625)	1.706 (1.710)	1.409 (1.404)	1.486 (1.495)	2.546	107.56 (112.13)	114.17 (118.43)	127.68 (125.39)	180.0 (0.0)
6-311G	1.639 (1.619)	1.693 (1.695)	1.416 (1.407)	1.478 (1.490)	2.538	107.01 (111.35)	114.22 (118.80)	128.43 (125.57)	180.0 (0.0)
6-31+G*	1.503 (1.497)	1.647 (1.646)	1.357 (1.348)	1.478 (1.485)	2.587	111.61 (114.23)	115.28 (120.15)	127.59 (123.97)	180.0 (0.0)
6-31+G**	1.496 (1.491)	1.648 (1.645)	1.347 (1.337)	1.479 (1.486)	2.564	111.82 (114.47)	115.93 (120.94)	126.74 (122.62)	180.0 (0.0)
6-311+G**	1.489 (1.483)	1.646 (1.644)	1.347 (1.336)	1.473 1.481)	2.564	111.85 (114.76)	116.05 (121.32)	126.85 (122.57)	180.0 (0.0)
6-311+G*	1.494 (1.488)	1.647 (1.645)	1.350 (1.340)	1.479 (1.487)	2.544	111.23 (114.05)	115.98 (120.70)	126.72 (123.15)	180.0 (0.0)
TZV	1.636 (1.617)	1.698 (1.701)	1.410 (1.398)	1.476 (1.488)	2.593	107.93 (112.64)	114.14 (119.07)	128.88 (124.90)	180.0 (0.0)
DZV	1.626 (1.609)	1.708 (1.711)	1.432 (1.422)	1.503 (1.514)	2.573	107.40 (112.32)	114.76 (118.98)	127.99 (125.57)	180.0 (0.0)
(B3LYP)									
6-311G**	1.508 (1.501)	1.650 (1.648)	1.344 (1.333)	1.475 (1.485)	2.55	110.75 (113.72)	115.90 (120.70)	126.92 (123.27)	180.0 (0.0)

Values in parenthesis refer to Z-form.

Table (13) : Total energy, net charges, bond orders and dipole moment of the two isomers of sulfine (FCH_3CSO) calculated at different levels and basis sets.

	T.E (Hartree)	Charges					Bond orders					Dipoles moment (Debye)
		O	S	C_3	F	C_5	S=O	C=S	C_3-F	C_3-C_5	O-H_7	
(RHF)												
6-31G	-649.02805 (-649.01883)	-0.72 (-0.69)	0.72 (0.70)	0.17 (0.18)	-0.37 (-0.35)	-0.55 (-0.54)	0.96 (0.99)	1.54 (1.52)	0.78 (0.80)	0.90 (0.90)		4.29 (7.30)
6-311G	-649.12117 (-649.11203)	-0.67 (-0.65)	0.61 (0.58)	0.20 (0.23)	-0.34 (-0.32)	-0.56 (-0.56)	0.94 (0.95)	1.61 (1.54)	0.79 (0.83)	0.82 (0.82)		4.25 (7.26)
6-31+G*	-649.20364 (-649.19986)	-0.74 (-0.72)	0.70 (0.69)	0.24 (0.25)	-0.33 (-0.31)	-0.40 (-0.40)	1.36 (1.41)	1.59 (1.58)	0.86 (0.90)	0.96 (0.96)		3.36 (5.42)
6-31+G**	-649.22301 (-649.22189)	-0.67 (-0.65)	0.51 (0.49)	0.40 (0.40)	-0.31 (-0.29)	-0.38 (-0.37)	1.56 (1.61)	1.67 (1.66)	0.97 (1.01)	1.02 (1.03)		3.11 (4.91)
6-311+G**	-649.31804 (-649.31915)	-0.88 (-0.71)	0.81 (0.63)	0.22 (0.29)	-0.27 (-0.31)	-0.22 (-0.08)	1.40 (1.61)	1.71 (1.74)	0.99 (0.95)	1.01 (1.05)		3.07 (4.98)
6-311+G*	-649.28827 (-649.28447)	-0.70 (-0.68)	0.70 (0.69)	0.03 (0.06)	-0.24 (-0.22)	-0.23 (-0.24)	1.34 (1.38)	1.61 (1.58)	0.92 (0.96)	0.93 (0.94)		3.37 (5.60)
TZV	-649.14896 (-649.14202)	-0.68 (-0.64)	0.62 (0.58)	0.11 (0.16)	-0.25 (-0.23)	-0.51 (-0.51)	0.90 (0.93)	1.65 (1.56)	0.87 (0.91)	0.93 (0.95)		4.50 (7.49)
DZV	-649.08007 (-649.07252)	-0.73 (-0.69)	0.67 (0.64)	0.13 (0.15)	-0.27 (-0.24)	-0.54 (-0.53)	0.97 (0.98)	1.56 (1.50)	0.89 (0.92)	0.86 (0.87)		4.28 (7.37)

Values in parenthesis refer to Z-form.

Table (13) continue.

	T.E (Hartree)	Charges					Bond orders					Dipoles moment (Debye)
		O	S	C_3	F	C_5	S=O	C=S	C_3-F	C_3-C_5	O-H_7	
(MP2)												
6-31G	-649.53019 (-649.52395)	-0.69 (-0.65)	0.85 (0.84)	0.01 (0.02)	-0.31 (-0.30)	-0.47 (-0.47)	1.17 (1.24)	1.30 (1.23)	0.77 (0.79)	0.88 (0.88)		2.70 (5.52)
6-311G	-649.66655 (-649.66021)	-0.67 (-0.65)	0.81 (0.79)	0.02 (0.04)	-0.30 (-0.29)	-0.53 (-0.53)	1.13 (1.19)	1.32 (1.23)	0.78 (0.81)	0.80 (0.79)	0.05	2.65 (5.58)
6-31+G*	-649.97035 (-649.96767)	-0.58 (-0.56)	0.64 (0.62)	0.13 (0.14)	-0.28 (-0.26)	-0.40 (-0.40)	1.39 (1.43)	1.34 (1.32)	0.86 (0.89)	0.93 (0.93)		2.24 (4.19)
6-31+G**	-650.07089 (-650.07018)	-0.51 (-0.49)	0.44 (0.41)	0.29 (0.29)	-0.24 (-0.22)	-0.41 (-0.40)	1.58 (1.63)	1.42 (1.40)	0.99 (1.03)	0.98 (0.98)		2.19 (3.87)
6-311+G**	-650.22376 (-650.22268)	-0.55 (-0.53)	0.55 (0.52)	0.20 (0.21)	-0.26 (-0.25)	-0.19 (-0.18)	1.56 (1.60)	1.47 (1.47)	0.91 (0.95)	1.01 (1.00)		2.11 (3.93)
6-311+G*	-650.13464 (-650.13217)	-0.54 (-0.52)	0.65 (0.62)	-0.06 (-0.03)	-0.20 (-0.19)	-0.29 (-0.30)	1.37 (1.41)	1.35 (1.32)	0.91 (0.94)	0.90 (0.90)		2.13 (4.21)
TZV	-649.70567 (-649.70192)	-0.67 (-0.62)	0.81 (0.76)	-0.06 (-0.03)	-0.22 (-0.20)	-0.50 (-0.50)	1.08 (1.14)	1.41 (1.30)	0.83 (0.86)	0.87 (0.89)	0.05	2.84 (5.85)
DZV	-649.56924 (-649.56474)	-0.72 (-0.68)	0.84 (0.82)	-0.01 (-0.003)	-0.24 (-0.22)	-0.54 (-0.53)	1.15 (1.18)	1.30 (1.23)	0.88 (0.90)	0.82 (0.83)		2.48 (5.67)
(B3LYP)												
6-311G**	-651.30025 (-651.29682)	-0.55 (-0.53)	0.60 (0.57)	-0.04 (-0.01)	-0.18 (-0.16)	-0.27 (-0.29)						2.76 (4.76)

Values in parenthesis refer to Z-form.

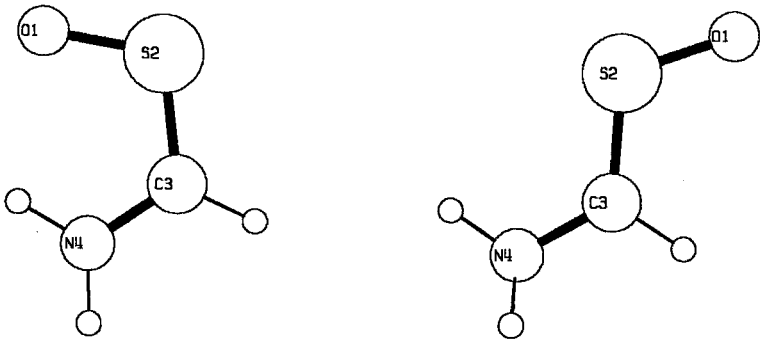
Table (12) contains the ground state geometrical parameters for the best geometry calculated at the three levels RHF, MP2 and B3LYP. These results show that the two forms are coplanar and the Z-conformer is higher in energy than its E-one, the difference in their stability is 0.70, 0.68 and 2.15 kcal/mol, respectively. Therefore, the electrostatic attraction between the positively methyl hydrogen atom and the negative terminal oxygen atom is the factor that stabilizes the E-form and thus, the formed pseudo aromatic cycle. Also, the σ-orbital-orbital interaction is another factor that favors 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, tables (1,4,8).

On the other hand, the angle CSO alters to avoid the repulsion interaction between negative flour and oxygen atoms (increase in case of Z-form). The same trend can be noticed for the angles of both substituents with C-S bond.

Table (13) shows the charge distribution on different centers in both isomers. The most interesting features drawn from these results are as follows. The charges accumulated on S-O bond are the same as those of mono-substituent, tables (3,5,9) which is higher than the unsubstituted parent sulfine. The second result is the attraction of negative charge on carbon atom of sulfine group to the electronegative fluorine atom, i.e. the

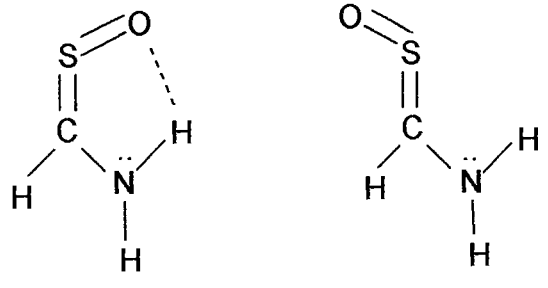
main factor influencing the charge distribution on sulfine is the strength of electronegativity of the substituent.

3.1.6. THIOAMIDE S-OXIDE



Z-form E-form

If one hydrogen atom of the parent sulfine is replaced by NH_2 group, the two conformers Z- and E- were optimized to the least energy stationary point and the results are given in tables (14,15). The calculations show the Z-isomer is found to be less in energy by 8.28, 8.85 and 9.14 kcal/mol at HF/6-311+G**, MP2/6-311+G** and B3LYP/6-311G**, respectively.



Z form E form

(hydrogen bonding)

Table (14) : Geometrical parameters of the two isomers of sulfine (NH_2CHSO) calculated at different levels and basis sets.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C=S	C-N	C-H	O-H_6	CSO	NCS	HCS	
(RHF)									
6-31G	1.762 (1.776)	1.722 (1.698)	1.298 (1.316)	1.071 (1.074)	1.949	96.09 (99.30)	119.12 (126.95)	120.71 (115.05)	0.0 (179.89)
6-311G	1.769 (1.788)	1.709 (1.686)	1.298 (1.317)	1.070 (1.071)	1.980	96.38 (99.15)	119.84 (127.21)	120.31 (115.21)	0.0 (179.89)
6-31+G*	1.507 (1.494)	1.636 (1.631)	1.321 (1.341)	1.075 (1.077)	2.272	106.31 (110.36)	121.11 (126.19)	119.45 (116.94)	0.0 (-178.83)
6-31+G**	1.491 (1.475)	1.628 (1.618)	1.324 (1.357)	1.073 (1.075)	2.344	107.60 (111.55)	122.22 (125.67)	118.43 (117.32)	0.0 (-175.67)
6-311+G**	1.482 (1.468)	1.624 (1.616)	1.327 (1.358)	1.072 (1.074)	2.371	108.17 (111.74)	122.61 (125.60)	118.01 (117.38)	-1.23 (-175.79)
6-311+G*	1.505 (1.491)	1.635 (1.626)	1.321 (1.348)	1.076 (1.077)	2.256	105.90 (110.07)	120.98 (126.21)	119.36 (116.76)	0.0 (-177.23)
TZV	1.749 (1.774)	1.719 (1.698)	1.296 (1.314)	1.070 (1.072)	2.007	96.91 (99.94)	119.62 (126.74)	120.74 (116.11)	0.0 (179.89)
DZV	1.748 (1.775)	1.706 (1.687)	1.311 (1.330)	1.070 (1.073)	2.019	97.15 (99.96)	120.00 (126.93)	120.37 (115.86)	0.0 (179.90)

Values in parenthesis refer to E-form.

Table (14) continue.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angle (Degree)
	S=O	C=S	C-N	C-H	O-H_6	CSO	NCS	HCS	
(MP2)									
6-31G	1.732 (1.683)	1.750 (1.714)	1.329 (1.361)	1.084 (1.090)	1.757	96.21 (106.08)	114.67 (126.09)	121.79 (115.44)	0.0 (179.97)
6-311G	1.731 (1.687)	1.739 (1.701)	1.326 (1.360)	1.081 (1.086)	1.760	96.34 (104.98)	114.77 (126.67)	121.52 (115.00)	0.0 (179.98)
6-31+G*	1.526 (1.505)	1.651 (1.646)	1.348 (1.388)	1.081 (1.084)	2.177	106.32 (113.12)	117.99 (123.98)	121.19 (118.54)	0.0 (-172.91)
6-31+G**	1.521 (1.498)	1.653 (1.647)	1.348 (1.392)	1.080 (1.084)	2.175	106.37 (113.53)	117.79 (123.60)	121.18 (118.72)	0.0 (-172.15)
6-311+G**	1.507 (1.490)	1.645 (1.644)	1.360 (1.389)	1.079 (1.082)	2.224	107.66 (113.39)	119.08 (123.58)	119.95 (118.65)	-3.83 (-172.26)
6-311+G*	1.518 (1.496)	1.649 (1.644)	1.349 (1.394)	1.084 (1.088)	2.149	106.14 (112.69)	117.54 (124.03)	121.19 (118.22)	0.0 (-172.31)
TZV	1.721 (1.686)	1.740 (1.707)	1.327 (1.358)	1.080 (1.084)	1.827	97.19 (106.27)	115.13 (125.90)	122.11 (116.53)	0.0 (179.97)
DZV	1.711 (1.673)	1.742 (1.712)	1.348 (1.383)	1.087 (1.095)	1.819	97.38 (106.12)	114.69 (126.08)	122.36 (116.55)	0.0 (179.97)
(B3LYP)									
6-311G**	1.536 (1.519)	1.667 (1.665)	1.338 (1.357)	1.082 (1.085)	2.17	105.43 (110.97)	118.17 (116.86)	120.76 (125.86)	0.0 (180.0)

Values in parenthesis refer to E-form.

Table (15) : Total energy , net charges , bond orders and dipole moment of the two isomers of (NH_2CHSO) calculated at different levels and basis sets.

	T.E (Hartree)	Charges					Bond orders					Dipole moment (Debye)
		O	S	C	N	H	S=O	C=O	C-N	C-H	$O-H_6$	
(RHF)												
6-31G	-566.23450 (-566.21874)	-0.79 (-0.72)	0.56 (0.53)	-0.12 (-0.11)	-0.79 (-0.82)	0.25 (0.29)	0.94 (0.92)	1.25 (1.35)	1.28 (1.11)	0.91 (0.90)	0.10	7.24 (8.92)
6-311G	-566.30126 (-566.28571)	-0.75 (-0.67)	0.45 (0.43)	-0.04 (-0.05)	-0.74 (-0.76)	0.24 (0.27)	0.93 (0.89)	1.30 (1.40)	1.25 (1.09)	0.90 (0.89)	0.09	7.27 (8.91)
6-31+G*	-566.36823 (-566.35470)	-0.81 (-0.78)	0.61 (0.61)	-0.01 (-0.03)	-0.67 (-0.69)	0.19 (0.22)	1.25 (1.30)	1.46 (1.50)	1.19 (1.08)	0.94 (0.94)		5.89 (7.06)
6-31+G**	-566.38502 (-566.37191)	-0.74 (-0.70)	0.44 (0.47)	0.07 (0.07)	-0.43 (-0.48)	0.15 (0.16)	1.47 (1.53)	1.53 (1.61)	1.28 (1.14)	0.96 (0.95)		5.50 (6.00)
6-311+G**	-566.45602 (-566.44282)	-0.79 (-0.75)	0.55 (0.58)	0.09 (0.07)	-0.28 (-0.29)	0.06 (0.05)	1.47 (1.53)	1.61 (1.69)	1.27 (1.15)	1.00 (1.00)	0.05	5.46 (6.02)
6-311+G*	-566.43056 (-566.41608)	-0.77 (-0.73)	0.59 (0.61)	-0.06 (-0.11)	-0.45 (-0.45)	0.15 (0.18)	1.23 (1.27)	1.47 (1.54)	1.23 (1.11)	0.95 (0.95)	0.05	5.98 (6.97)
TZV	-566.32122 (-566.30482)	-0.75 (-0.68)	0.44 (0.43)	-0.07 (-0.09)	-0.66 (-0.65)	0.24 (0.27)	0.90 (0.86)	1.32 (1.45)	1.35 (1.20)	0.89 (0.88)		7.53 (9.31)
DZV	-566.26487 (-566.24828)	-0.79 (-0.71)	0.51 (0.47)	-0.18 (-0.17)	-0.66 (-0.68)	0.26 (0.30)	0.95 (0.92)	1.33 (1.40)	1.26 (1.13)	0.90 (0.89)	0.08	7.38 (9.12)

Values in parenthesis refer to E-form.

Table (15) continue.

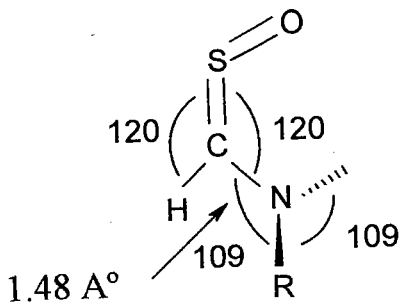
	T.E (Hartree)	Charges					Bond orders					Dipole moment (Debye)
		O	S	C	N	H	S=O	C=O	C-N	C-H	O-H_6	
(MP2)												
6-31G	-566.62113 (-566.59992)	-0.78 (-0.75)	0.64 (0.70)	-0.21 (-0.22)	-0.65 (-0.71)	0.21 (0.24)	0.95 (1.07)	1.23 (1.31)	1.24 (1.00)	0.89 (0.89)	0.19	6.13 (7.99)
6-311G	-566.72126 (-566.69959)	-0.76 (-0.73)	0.58 (0.66)	-0.17 (-0.21)	-0.63 (-0.67)	0.23 (0.24)	0.95 (1.02)	1.24 (1.34)	1.21 (0.97)	0.87 (0.87)	0.17	6.14 (8.08)
6-31+G*	-566.99174 (-566.97888)	-0.67 (-0.60)	0.59 (0.61)	-0.12 (-0.16)	-0.60 (-0.60)	0.16 (0.18)	1.28 (1.38)	1.33 (1.34)	1.11 (0.98)	0.90 (0.90)	0.07	4.48 (4.90)
6-31+G**	-567.06345 (-567.05056)	-0.59 (-0.53)	0.40 (0.42)	-0.04 (-0.04)	-0.36 (-0.43)	0.12 (0.13)	1.48 (1.59)	1.37 (1.43)	1.22 (1.07)	0.92 (0.91)	0.08	4.26 (4.47)
6-311+G**	-567.17060 (-567.15649)	-0.61 (-0.57)	0.51 (0.52)	-0.05 (-0.05)	-0.25 (-0.27)	0.06 (0.05)	1.48 (1.57)	1.45 (1.48)	1.17 (1.07)	0.95 (0.94)	0.08	3.94 (4.56)
6-311G*	-567.09870 (-567.08604)	-0.62 (-0.56)	0.59 (0.62)	-0.20 (-0.27)	-0.40 (-0.38)	0.14 (0.16)	1.26 (1.36)	1.33 (1.36)	1.13 (1.00)	0.91 (0.90)	0.08	4.41 (4.76)
TZV	-566.74997 (-566.72713)	-0.77 (-0.73)	0.57 (0.66)	-0.20 (-0.25)	-0.58 (-0.60)	0.23 (0.24)	0.92 (0.96)	1.29 (1.43)	1.26 (1.05)	0.85 (0.86)	0.10	6.45 (8.54)
DZV	-566.65033 (-566.62688)	-0.80 (-0.77)	0.63 (0.71)	-0.28 (-0.32)	-0.57 (-0.60)	0.24 (0.26)	0.95 (1.02)	1.27 (1.35)	1.21 (1.00)	0.87 (0.87)	0.16	6.14 (8.18)
(B3LYP)												
6-311G**	-568.09932 (-568.08474)	-0.62 (-0.58)	0.51 (0.51)	-0.14 (-0.17)	-0.38 (-0.40)	0.14 (0.15)						4.94 (6.38)

Values in parenthesis refer to E-form.

The best conformer of the two isomers is found to be planar structure (at least for all atoms other than hydrogens, NH_2) and the N atom is in its sp^2 hyperdization in case of the Z-form while it is pyrimedilized one in the E-isomer.

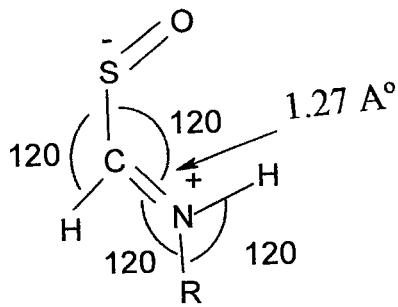
Table (14) presents the geometrical parameters of the ground state of both E- and Z-isomers. As shown in this table, the S-O bond of Z-form is longer by $\approx$ 0.01 A° than the corresponding E-isomer, while the C—S bonds are of the same length. The difference in length between the two C—N bonds is 0.03 A ° , where C—N of the Z-form is shorter. These bond lengths are midway between the two contributing resonance forms (**A**,**B**). These noticeable differences are attributed to internal difference in bonding nature of the two isomers. The delocalization of nitrogen lone-pair of electrons in the Z-form is more clear than in case of the E-isomer.

In other words, the C—N bond has partial double bond character in both isomers but it is extent is higher in Z-form, which resulting from the delocalization of the nitrogen lone-pair electrons into the π-system of the CSO group. Consequently, one expects the existence of configuration isomers (cis and trans) depending on the rotational barrier about the C—N bond.



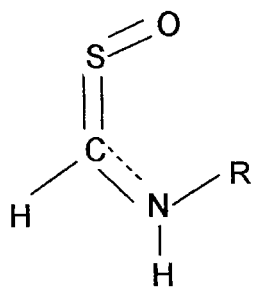
(A)

(Zero conjugation)

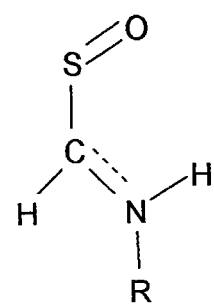


(B)

(Complete conjugation)



(Cis)



(Trans)

The decrease of CSO and SCN angles values of the Z-isomers (the difference is 3 °) is attributed to the existence of electrostatic attraction between the terminal oxygen atom and H_5 atoms. The total bond order of C—N bond comparing to the parent sulfine, $-NH_2$ group causes the greatest effect of the ground state properties of sulfine. The C-S and S-O bonds elongates by 0.04 A° while CSO angle decreases from 115.4 ° (the parent) to 108.2 ° at Z-isomer. On the other hand, the atomic charge distribution on CSO group remarkably changes, table (15), the negative charge on the terminal S-O group increases, which leads to more electrostatic attraction between the terminal oxygen atom and H_5. Another interesting result of all levels of calculation is the decrease of the

polarizability of C-S bond due to decrease of negative charge on carbon atom, while the charge on terminal oxygen atom increases.

The main factor contribute to the stability of Z-form over its E-isomer is the electrostatic interaction between negatively charged oxygen atom (-0.79) and the nearest hydrogen atom (0.17) and consequently the cyclic forms arising. The distance of O.....H is calculated as 2.37, 2.22 and 2.17 A ° at the HF, MP2 and B3LYP levels, respectively. Another factor that stabilizes the Z-form is the σ-stabilization. These factors are missed in the E-isomer.

The change of relative total energy during rotation of $-NH_2$ group around C—N bond with rotational angle ϕ (dihedral angle of H_5) is shown in figure (1). The rotational barrier is calculated to be 9.95 kcal/mol at the MP2 level. The least stable conformer has ϕ = 60 ° , which has "-566.97587" a ($O...H_5$) distance (2.94 A°) and decrease the net charge on oxygen atom (-0.57) leading to minimum electrostatic attraction.

The calculation predications that both the C-S and S-O bonds decreased upon rotation and hence increase the double bond character and reaches it smallest value at ϕ = 60 ° . On the other hand, the C—N bond elongates, leading to less double character from 1.348 A ° at ϕ = 0 ° conformer to 1.420 A ° at ϕ = 60 °. This is attributed to the loss of conjugation during rotation.

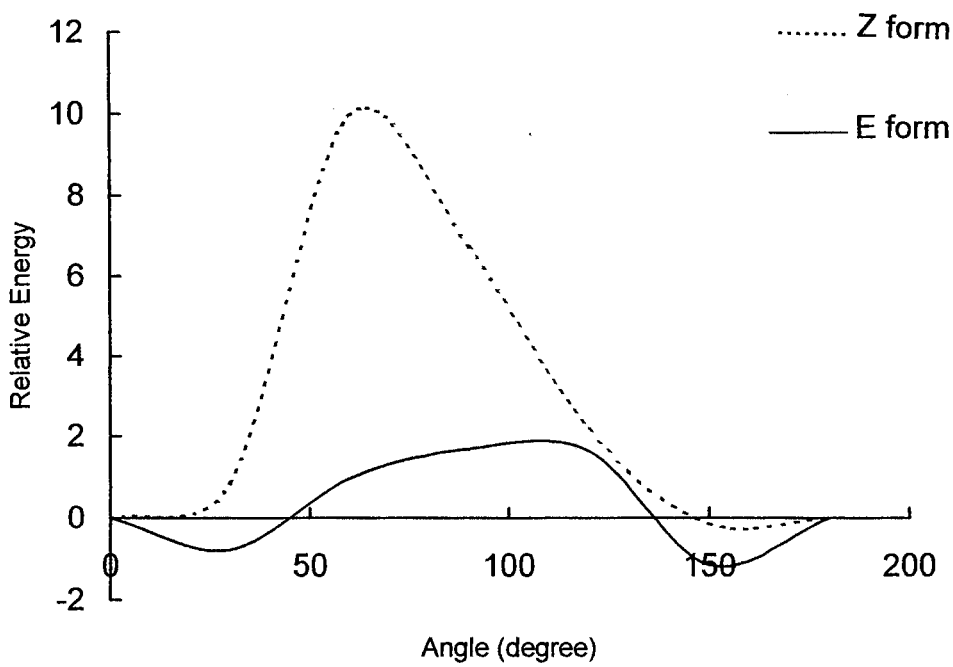
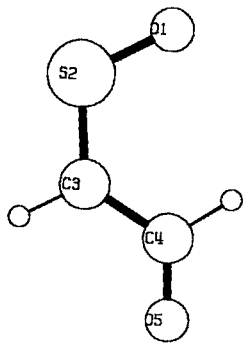
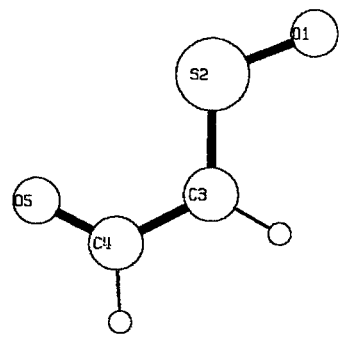


Fig. (1): Variation of total energy of Z- and E-thioamide S-oxide with different dihedral angle calculated at MP2/6-31G* level.

3.1.7. THIOXOETHANAL S-OXIDE



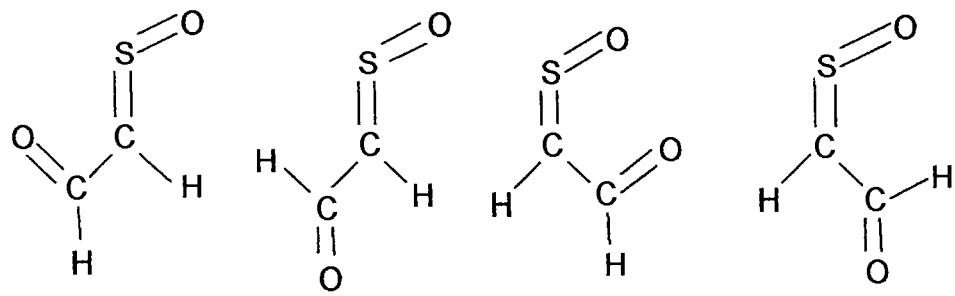
Z-form



E-form

If hydrogen atom of sulfine is replaced by formyl group (CHO), thioxoethanal S-oxide is obtained. The structure of Z- and E-isomers of thioxoethanal S-oxide were optimized at the same levels of calculations and the results are given in tables (16,17). It is clear that the Z-isomer is more stable than E-form, the difference in total energy is 2.57, 4.83 and 1.07 kcal/mol at the HF/6-311+G**, MP2/6-311+G** and B3LYP/6-311G** levels, respectively. The distance $O_1 \ldots H_6$ is found to be 2.66 A° in case Z-isomer (**A**). The electrostatic interaction (attraction) and the formed five membered cycle (**A**) stabilize the Z-form over the E-one (**C**,**D**) and the Z-form (**B**).

The form (**B**) is also destabilized by the electrostatic repulsion between the oxygen atoms (-0.42,-0.25). The difference in energy between these forms is found to be 0.0, 2.26, 0.94, 0.56 kcal/mol for forms **A**, **B**, **C**, **D**, at MP2/6-311+G* respectively.



(D) **(C)** **(B)** **(A)**

The two isomers are coplanar and the different bond lengths are appreciably of the same length in the two forms (E- and Z-) while the bond angles differ to avoid the steric hindrances and repulsion between atoms of similar charges. Comparing to the parent sulfine, the C-S bond length elongates by 0.02 A° and the CSO angle decreases by 3°, due to the electrostatic interaction between terminal oxygen and the aldehydic hydrogen atom.

Table (17) shows the Mulliken atomic charges on the different centers and total bond order of various bonds in both forms. The atomic charge on the sulfinic oxygen atom of Z-isomer is greater than that of the E-form, and the reverse is found for the S atom, while the other atoms have nearly the same charges in both isomers. The charge distribution of CSO group is appreciably changed upon substitution by –COH group. The substitution increases the S-C bond polarizability, the sulfur atom becomes more positive in both isomers and the negative charge on carbon atom increases only in case of Z-isomer while the charge on the terminal oxygen atom does not affect by the substitution.

Table (16) : Geometrical parameters of the two isomers of sulfine (CHOCHSO) calculated at different levels and basis sets.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C_3=S	C_3-C_4	C_3-H_7	O-H_6	CSO	C_4C_3S	HCS	
(RHF)									
6-31G	1.677 (1.656)	1.642 (1.643)	1.473 (1.469)	1.072 (1.072)	2.518	107.65 (107.27)	123.92 (122.88)	118.12 (117.54)	0.0 (180.0)
6-311G	1.684 (1.661)	1.631 (1.631)	1.473 (1.470)	1.069 (1.070)	2.520	107.33 (106.72)	124.44 (123.23)	118.09 (117.36)	0.0 (180.0)
6-31+G*	1.456 (1.452)	1.593 (1.598)	1.483 (1.481)	1.076 (1.076)	2.676	114.44 (113.44)	125.61 (120.07)	115.76 (119.67)	0.0 (180.0)
6-31+G**	1.444 (1.441)	1.589 (1.593)	1.483 (1.483)	1.074 (1.073)	2.669	114.80 (113.59)	125.47 (119.46)	115.55 (119.79)	0.0 (180.0)
6-311+G**	1.438 (1.435)	1.589 (1.592)	1.481 (1.481)	1.072 (1.072)	2.674	114.95 (113.64)	125.46 (119.72)	115.44 (119.84)	0.0 (180.0)
6-311+G*	1.451 (1.447)	1.592 (1.596)	1.486 (1.484)	1.076 (1.076)	2.658	114.12 (113.07)	125.49 (120.20)	115.65 (119.52)	0.0 (180.0)
TZV	1.667 (1.648)	1.637 (1.637)	1.476 (1.472)	1.070 (1.070)	2.558	108.24 (107.54)	124.58 (123.17)	117.90 (117.96)	0.0 (180.0)
DZV	1.662 (1.641)	1.636 (1.638)	1.485 (1.481)	1.071 (1.072)	2.524	107.42 (106.78)	124.24 (123.64)	118.39 (117.85)	0.0 (180.0)

Values in parenthesis refer to E-form.

Table (16) continue.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C_3=S	C_3-C_4	C_3-H_7	O-H_6	CSO	C_4C_3S	HCS	
(MP2)									
6-31G	1.607 (1.608)	1.745 (1.761)	1.452 (1.450)	1.089 (1.089)	2.721	111.72 (109.12)	124.55 (118.30)	112.66 (116.93)	0.0 (180.0)
6-311G	1.599 (1.600)	1.735 (1.751)	1.446 (1.445)	1.085 (1.085)	2.714	111.25 (108.40)	125.00 (118.68)	112.49 (116.32)	0.0 (180.0)
6-31+G*	1.497 (1.500)	1.647 (1.652)	1.464 (1.465)	1.084 (1.083)	2.678	114.19 (112.80)	124.92 (118.59)	114.70 (119.30)	0.0 (180.0)
6-31+G**	1.488 (1.491)	1.644 (1.650)	1.468 (1.470)	1.084 (1.083)	2.675	114.55 (113.18)	124.88 (117.68)	114.58 (119.52)	0.0 (180.0)
6-311+G*	1.487 (1.489)	1.646 (1.651)	1.469 (1.470)	1.088 (1.087)	2.675	114.05 (112.39)	125.11 (118.77)	114.39 (118.92)	0.0 (180.0)
TZV	1.597 (1.598)	1.738 (1.755)	1.443 (1.444)	1.085 (1.084)	2.774	112.19 (109.21)	125.61 (118.96)	112.18 (117.14)	0.0 (180.0)
DZV	1.594 (1.595)	1.749 (1.768)	1.471 (1.469)	1.093 (1.095)	2.719	111.19 (108.43)	124.63 (119.44)	113.09 (117.17)	0.0 (180.0)
(B3LYP)									
6-311G**	1.492	1.637	1.470	1.085	2.689	113.92	125.79	114.85	0.0

Values in parenthesis refer to E-form.

Table (17) : Total energy, net charges, bond orders and dipole moment of the two isomers of sulfine (CHOCHSO) calculated at different levels and basis sets.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	H_7	S=O	C=S	C_3-C_4	C_3-H_7	
(RHF)											
6-31G	-623.84372 (-623.83877)	-0.74 (-0.73)	0.88 (0.96)	-0.56 (-0.59)	0.33 (0.33)	0.29 (0.30)	1.07 (1.10)	1.62 (1.62)	0.92 (0.89)	0.89 (0.89)	3.53 (3.95)
6-311G	-623.92713 (-623.92194)	-0.71 (-0.70)	0.78 (0.87)	-0.52 (-0.57)	0.35 (0.36)	0.28 (0.29)	1.04 (1.07)	1.63 (1.63)	0.88 (0.83)	0.88 (0.88)	3.56 (3.92)
6-31+G*	-624.04356 (-624.04050)	-0.68 (-0.66)	0.83 (0.89)	-0.46 (-0.49)	0.38 (0.38)	0.22 (0.22)	1.48 (1.50)	1.59 (1.59)	0.97 (0.97)	0.93 (0.93)	2.59 (2.65)
6-31+G**	-624.06521 (-624.06129)	-0.60 (-0.59)	0.62 (0.70)	-0.24 (-0.27)	0.30 (0.30)	0.17 (0.15)	1.66 (1.69)	1.68 (1.68)	1.01 (1.01)	0.95 (0.95)	2.30 (2.64)
6-311+G**	-624.15129 (-624.14713)	-0.67 (-0.66)	0.79 (0.83)	-0.20 (-0.20)	0.36 (0.35)	0.07 (0.04)	1.65 (1.68)	1.72 (1.70)	1.02 (1.02)	0.99 (1.00)	2.37 (2.61)
6-311+G*	-624.12053 (-624.11698)	-0.64 (-0.62)	0.84 (0.90)	-0.47 (-0.51)	0.33 (0.34)	0.19 (0.19)	1.46 (1.47)	1.59 (1.58)	0.94 (0.94)	0.94 (0.95)	2.70 (2.61)
TZV	-623.94957 (-623.94421)	-0.69 (-0.67)	0.76 (0.85)	-0.48 (-0.56)	0.29 (0.33)	0.27 (0.29)	1.01 (1.04)	1.64 (1.68)	0.97 (0.95)	0.87 (0.86)	3.62 (4.11)
DZV	-623.88521 (-623.87956)	-0.76 (-0.75)	0.84 (0.92)	-0.50 (-0.54)	0.17 (0.17)	0.28 (0.31)	1.06 (1.09)	1.60 (1.61)	0.88 (0.84)	0.89 (0.89)	3.62 (4.00)

Values in parenthesis refer to E-form.

Table (17) continue.

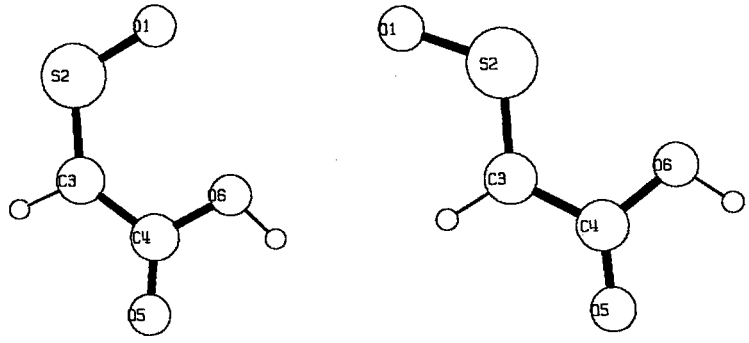
	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	H_7	S=O	C=S	C_3-C_4	C_3-H_7	
(MP2)											
6-31G	-624.36549 (-624.36800)	-0.57 (-0.54)	0.88 (0.89)	-0.57 (-0.56)	0.26 (0.25)	0.22 (0.23)	1.35 (1.35)	1.11 (1.09)	0.97 (0.96)	0.88 (0.88)	3.33 (1.85)
6-311G	-624.48837 (-624.49055)	-0.56 (-0.53)	0.84 (0.86)	-0.58 (-0.58)	0.26 (0.25)	0.24 (0.24)	1.31 (1.31)	1.10 (1.04)	0.94 (0.91)	0.85 (0.86)	3.37 (1.65)
6-31+G*	-624.80488 (-624.80435)	-0.51 (-0.50)	0.70 (0.73)	-0.41 (-0.42)	0.29 (0.27)	0.19 (0.19)	1.47 (1.47)	1.29 (1.29)	0.97 (0.96)	0.88 (0.89)	2.48 (1.99)
6-31+G**	-624.89220 (-624.89089)	-0.44 (-0.44)	0.52 (0.56)	-0.24 (-0.24)	0.21 (0.19)	0.15 (0.13)	1.65 (1.65)	1.39 (1.38)	0.99 (0.99)	0.90 (0.91)	2.24 (2.03)
6-311+G**[a]	-625.01555 (-625.01306)	-0.67 (-0.66)	0.79 (0.83)	-0.20 (-0.20)	0.36 (0.35)	0.07 (0.04)	1.65 (1.68)	1.72 (1.70)	1.02 (1.02)	0.99 (1.00)	2.37 (2.61)
6-311+G*	-624.94367 (-624.94274)	-0.46 (-0.45)	0.71 (0.74)	-0.46 (-0.47)	0.21 (0.20)	0.17 (0.17)	1.46 (1.45)	1.28 (1.29)	0.95 (0.93)	0.89 (0.90)	2.53 (1.72)
TZV	-624.52342 (-624.52466)	-0.53 (-0.49)	0.81 (0.82)	-0.56 (-0.58)	0.19 (0.20)	0.24 (0.27)	1.27 (1.28)	1.13 (1.13)	1.03 (1.00)	0.83 (0.83)	3.42 (1.82)
DZV	-624.39817 (-624.40005)	-0.59 (-0.55)	0.85 (0.85)	-0.53 (-0.53)	0.11 (0.09)	0.24 (0.26)	1.29 (1.30)	1.11 (1.09)	0.93 (0.91)	0.86 (0.87)	3.58 (1.77)
(B3LYP)											
6-311G**	-626.06336	-0.49	0.68	-0.41	0.20	0.17					2.53

Values in parenthesis refer to E-form.

[a] Single point calculations.

3.1.8. THIOXOACETIC S-OXIDE

Molecular orbital calculation performed on both Z- and E-isomers of thioxoacetic S-oxide show that the two forms are also planar and have nearly the same bond lengths while only two bond angles differ, where CSO angle of Z-form is greater by 4° than that of E-one and the SCC angle of E-form decreases by 10°, table (18).



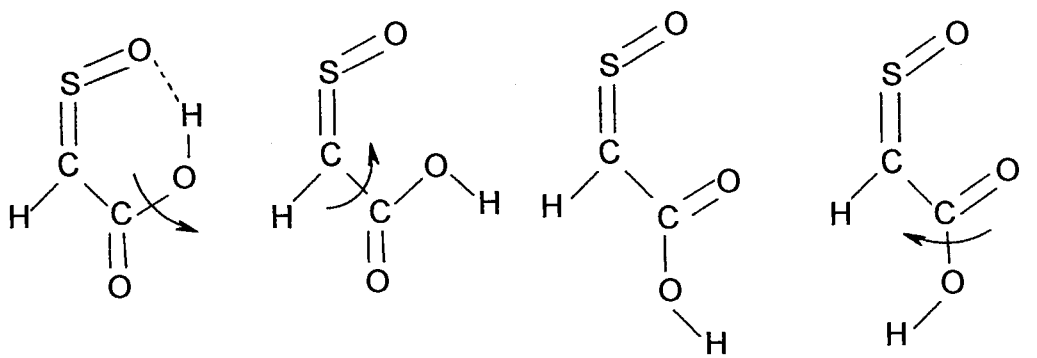
Z-form E-form

Replacement of one hydrogen atom in sulfine by carboxylic group elongates only C-S bond 0.01 A°. Many rotomers for this compound can be drawn by either the rotation of the carboxylic group around C_3-C_4 bond or by rotation of –OH group around C_4-O_5 bond. The most stable conformers are shown below

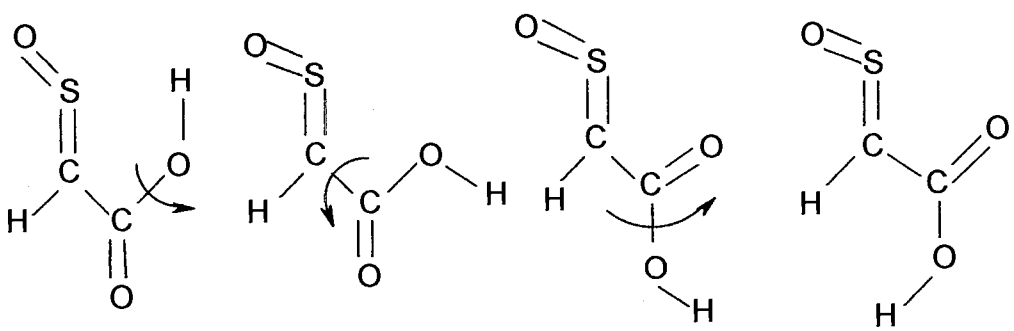
The electrostatic interactions (repulsion or attraction) and so the formed hydrogen bonds are the main factors determined the relative stability of such conformers. In case of Z-isomer, it's found that conformer (**A**) is the most stable one while the highest energy one is (**D**), indicating that electrostatic attraction is the major factor. The hydrogen

bond formed between sulfinic oxygen atom and carboxylic hydrogen is 1.79 A ° and thus six membered cyclic form is formed.

The Z-structure of thioxoacetic S-oxide 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 HF/6-311+G**, MP2/6-311+G** and B3LYP/6-311G**, respectively.



(A) **(B)** **(C)** **(D)**



(Ȧ) **(Ḃ)** **(Ċ)** **(Ḋ)**

The carboxylic group increases the charges on S-O bond in the two isomers, and therefore increases its polarizability. The charge on carbon atom is not appreciably affected by the presence of carboxylic group, table (19). This means that the electron withdrawing effect of S=O bond retards that of carboxylic group.

Table (18) : Geometrical parameters of the two isomers of sulfine (HCOOHCSO) calculated at different levels and basis sets.

	Bond lengths (Angstrom)				Bond angles (Degree)			Twist angle (Degree)
	S=O	C=S	C_3-C_4	C_3-H_8	CSO	C_4C_3S	HC_3S	
(RHF)								
6-31G	1.678 (1.655)	1.635 (1.639)	1.482 (1.465)	1.072 (1.071)	108.07 (107.25)	124.54 (123.97)	117.96 (118.98)	-0.17 (180.0)
6-311G	1.689 (1.659)	1.623 (1.627)	1.481 (1.465)	1.069 (1.068)	106.94 (106.82)	124.36 (124.24)	118.21 (118.90)	0.40 (180.0)
6-31+G*	1.446 (1.451)	1.594 (1.595)	1.482 (1.479)	1.075 (1.074)	117.88 (113.33)	132.11 (122.38)	112.77 (120.53)	0.0 (180.0)
6-31+G**	1.436 (1.440)	1.590 (1.591)	1.483 (1.479)	1.073 (1.071)	117.85 (113.58)	132.03 (121.68)	112.54 (120.90)	0.0 (180.0)
6-311+G**	1.430 (1.434)	1.589 (1.590)	1.481 (1.477)	1.072 (1.070)	117.94 (113.64)	131.94 (121.68)	112.49 (121.00)	0.0 (180.0)
6-311+G*	1.441 (1.447)	1.593 (1.594)	1.484 (1.481)	1.075 (1.074)	117.63 (112.95)	132.32 (122.37)	112.47 (120.43)	0.0 (180.0)
TZV	1.670 (1.646)	1.631 (1.633)	1.485 (1.468)	1.070 (1.069)	108.43 (107.65)	125.29 (123.95)	117.69 (119.69)	0.39 (180.0)
DV	1.663 (1.639)	1.629 (1.634)	1.495 (1.476)	1.070 (1.071)	107.65 (106.90)	124.50 (124.24)	118.43 (119.40)	-0.67 (180.0)

Values in parenthesis refer to E-form.

Table (18) continue.

	Bond lengths (Angstrom)				Bond angles (Degree)			Twist angle (Degree)
	S=O	C=S	C_3-C_4	C_3-H_8	CSO	C_4C_3S	HC_3S	
(MP2)								
6-31G	1.601 (1.607)	1.761 (1.757)	1.449 (1.449)	1.089 (1.087)	115.76 (108.81)	130.87 (120.71)	109.81 (117.52)	0.0 (180.0)
6-311G	1.593 (1.599)	1.750 (1.745)	1.443 (1.442)	1.085 (1.083)	115.09 (108.23)	131.43 (120.92)	109.43 (117.16)	0.0 (180.0)
6-31+G*	1.494 (1.498)	1.648 (1.649)	1.468 (1.466)	1.083 (1.082)	117.00 (112.75)	130.99 (121.52)	112.00 (119.79)	0.0 (180.0)
6-311+G*	(1.487)	(1.648)	(1.469)	(1.086)	(112.36)	(121.58)	(119.54)	(180.0)
TZV	1.591 (1.598)	1.752 (1.749)	1.441 (1.442)	1.084 (1.082)	115.63 (109.16)	131.53 (120.55)	109.74 (118.39)	0.0 (180.0)
DZV	1.588 (1.595)	1.766 (1.763)	1.465 (1.465)	1.094 (1.094)	115.23 (108.21)	130.72 (120.77)	110.18 (117.91)	0.0 (180.0)
(B3LYP)								
6-311G**	(1.490)	(1.637)	(1.471)	(1.083)	(112.42)	(118.26)	(120.37)	(180.0)

Values in parenthesis refer to E-form.

Table (19) : Total energy, net charges, bond orders and dipole moment of the two isomers of sulfine (HCOOCHSO) calculated at different levels and basis sets.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	H_8	S=O	C_3=S	C_3-C_4	C_3-H_8	
(RHF)											
6-31G	-698.68359 (-698.69190)	-0.73 (-0.73)	0.89 (0.98)	-0.51 (-0.57)	0.77 (0.78)	0.30 (0.32)	1.08 (1.10)	1.67 (1.63)	0.87 (0.91)	0.88 (0.88)	4.50 (4.30)
6-311G	-698.79077 (-698.79846)	-0.70 (-0.70)	0.79 (0.88)	-0.46 (-0.54)	0.74 (0.77)	0.30 (0.31)	1.04 (1.07)	1.70 (1.63)	0.84 (0.86)	0.87 (0.88)	4.68 (4.44)
6-31+G*	-698.93363 (-698.93674)	-0.64 (-0.66)	0.84 (0.87)	-0.47 (-0.46)	0.78 (0.77)	0.23 (0.24)	1.54 (1.50)	1.56 (1.59)	0.99 (0.99)	0.93 (0.92)	1.47 (2.80)
6-31+G**	-698.95932 (-698.96273)	-0.56 (-0.59)	0.63 (0.67)	-0.26 (-0.25)	0.66 (0.66)	0.18 (0.17)	1.70 (1.68)	1.67 (1.69)	1.02 (1.03)	0.95 (0.95)	1.22 (2.41)
6-311+G**	-699.06530 (-699.06886)	-0.64 (-0.66)	0.79 (0.81)	-0.22 (-0.17)	0.51 (0.53)	0.08 (0.04)	1.71 (1.68)	1.69 (1.72)	1.05 (1.05)	0.99 (1.00)	1.27 (2.45)
6-311+G*	-699.03105 (-699.03424)	-0.61 (-0.62)	0.84 (0.89)	-0.48 (-0.49)	0.58 (0.58)	0.19 (0.20)	1.52 (1.47)	1.55 (1.59)	0.95 (0.96)	0.94 (0.95)	1.61 (2.94)
TZV	-698.82281 (-698.83051)	-0.67 (-0.67)	0.77 (0.86)	-0.47 (-0.54)	0.62 (0.64)	0.27 (0.29)	1.01 (1.04)	1.70 (1.69)	0.92 (0.95)	0.86 (0.87)	4.76 (4.52)
DZV	-698.74267 (-698.75048)	-0.75 (-0.74)	0.86 (0.93)	-0.50 (-0.57)	0.56 (0.57)	0.29 (0.33)	1.06 (1.09)	1.68 (1.59)	0.82 (0.85)	0.89 (0.89)	4.67 (4.49)

Values in parenthesis refer to E-form.

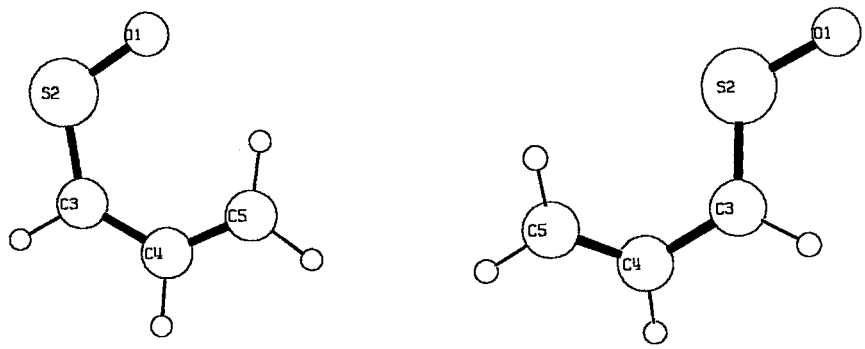
Table (19) continue.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	H_8	S=O	C_3=S	C_3-C_4	C_3-H_8	
(MP2)											
6-31G	-699.33770 (-699.34259)	-0.50 (-0.55)	0.86 (0.91)	-0.55 (-0.55)	0.57 (0.57)	0.22 (0.24)	1.38 (1.34)	1.05 (1.10)	0.97 (0.95)	0.89 (0.88)	1.65 (2.21)
6-311G	-699.49334 (-699.49906)	-0.50 (-0.54)	0.81 (0.87)	-0.55 (-0.57)	0.55 (0.56)	0.24 (0.26)	1.34 (1.30)	1.03 (1.09)	0.94 (0.91)	0.86 (0.86)	1.74 (2.35)
6-31+G*	-699.87352 (-699.87591)	-0.48 (-0.50)	0.69 (0.72)	-0.42 (-0.41)	0.59 (0.58)	0.19 (0.20)	1.50 (1.46)	1.27 (1.30)	0.98 (0.97)	0.89 (0.89)	1.10 (2.06)
6-31+G**	-698.89727 (-698.90301)	-0.65 (-0.68)	0.74 (0.77)	-0.29 (-0.27)	0.78 (0.78)	0.19 (0.20)	1.53 (1.51)	1.65 (1.67)	1.03 (1.03)	0.95 (0.95)	2.19 (2.69)
6-311+G**	-699.00702 (-699.01279)	-0.59 (-0.62)	0.68 (0.70)	-0.16 (-0.11)	0.56 (0.57)	0.10 (0.07)	1.60 (1.57)	1.66 (1.68)	1.08 (1.07)	0.99 (1.00)	2.29 (2.74)
6-311+G*	-698.97683 (-700.05832)	-0.61 (-0.45)	0.79 (0.73)	-0.41 (-0.46)	0.58 (0.39)	0.20 (0.19)	1.40 (1.44)	1.55 (1.29)	0.99 (0.93)	0.93 (0.90)	2.57 (2.11)
TZV	-699.54006 (-699.54542)	-0.46 (-0.50)	0.79 (0.83)	-0.57 (-0.56)	0.44 (0.43)	0.22 (0.26)	1.30 (1.27)	1.07 (1.16)	0.98 (0.99)	0.84 (0.84)	1.82 (2.38)
DZV	-699.38332 (-699.38896)	-0.52 (-0.56)	0.82 (0.86)	-0.55 (-0.56)	0.39 (0.39)	0.24 (0.28)	1.32 (1.29)	1.04 (1.08)	0.89 (0.89)	0.87 (0.88)	1.86 (2.37)
(B3LYP)											
6-311+G**	(-701.33797)	(-0.47)	(0.73)	(-0.41)	(0.36)	(0.18)					(2.43)

Values in parenthesis refer to E-form.

3.1.9. THIOACROLEIN S-OXIDE

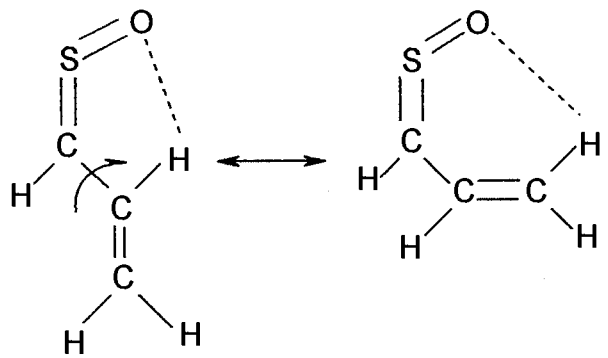
Sulfines (thiocarbonyl S-oxides) are generally more stable than the corresponding thioaldehydes or thioketons. The simplest thiocarbonyl S-oxide (thioacrolein S-oxide) was synthesized for the first time in two stereoisomers (E- and Z-) and its cyclic isomers was studied theoretically[35].



Z-form E-form

The vinyl group (C=C) is an electron withdrawing group and can participate in π-conjugation with CSO group. The resonating structures of thioacrolein S-oxide are shown below. So it is interesting to find out the effect of vinyl group on the properties of the sulfine group, specially its charge distribution and its polarizability. The rotation of the vinyl moiety around the C_3-C_4 bond results in two forms in both E- and Z-stereoisomers. All levels of calculations at 6-311+G** basis set show the conformer (**A**) to be little bit more stable (ΔE is only 2.0 kcal/mol) while

the barrier to internal rotation is calculated as 0.68 kcal/mol at MP2/6-311+G*.



(**A**) trans (**B**) cis

In both Z-forms (**A** and **B**) there exists an electrostatic attraction between oxygen atom of sulfine group and the nearest vinyl hydrogen atom, the distance O…H is 2.60 A° (case **A**) and 2.25 A° (case **B**).

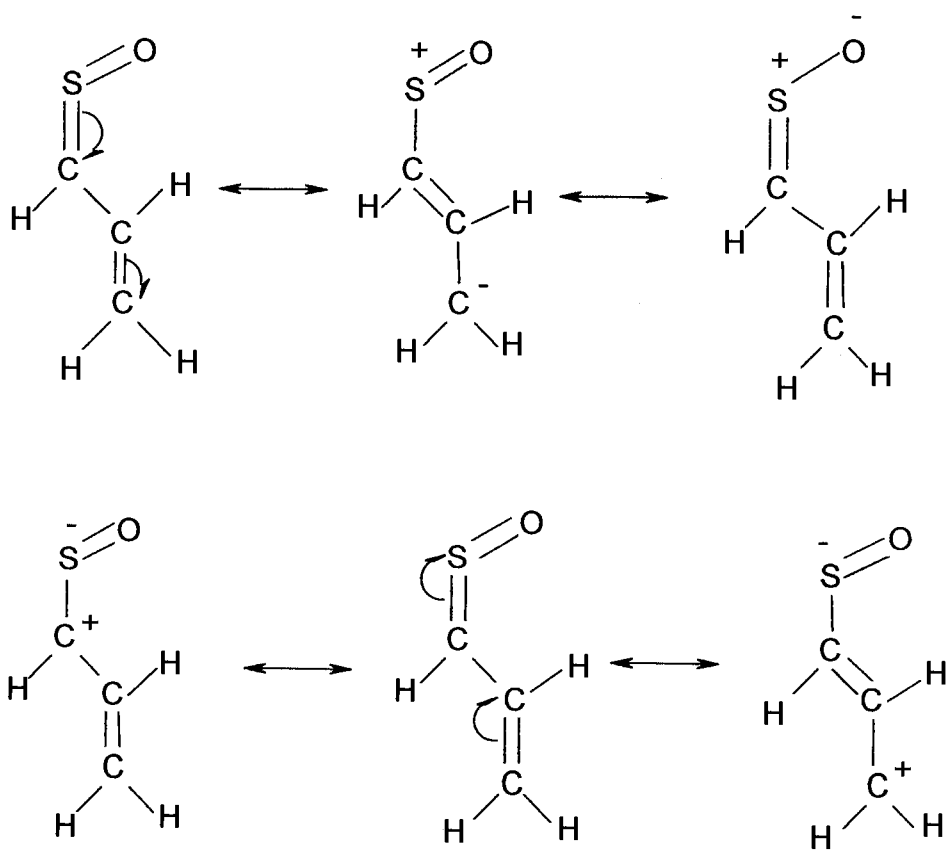


Table (20) : Geometrical parameters of the two isomers of sulfine (C_2H_3CHSO) calculated at different levels and basis sets.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C_3=S	C_3-C_4	C_3-H_9	O-H_6	CSO	C_4C_3S	H_9C_3S	
(RHF)									
6-31+G*	1.470 (1.464)	1.602 (1.599)	1.456 (1.468)	1.077 (1.077)	2.299	114.77 (113.94)	130.46 (122.10)	111.37 (118.06)	0.0 (177.94)
6-311+G*	1.466 (1.460)	1.601 (1.597)	1.457 (1.469)	1.078 (1.078)	2.279	114.35 (113.44)	130.43 (12218)	111.20 (117.82)	0.0 (178.08)
6-311+G**	1.451 (1.446)	1.595 (1.593)	1.457 (1.467)	1.074 (1.074)	2.330	115.41 (114.27)	130.93 (121.47)	110.56 (118.30)	0.0 (178.13)
(MP2)									
6-31+G*	1.501 (1.496)	1.643 (1.645)	1.447 (1.457)	1.085 (1.084)	2.267	114.98 (114.57)	129.02 (118.85)	110.75 (118.56)	0.0 (176.23)
6-311+G*	1.490 (1.486)	1.642 (1.644)	1.450 (1.460)	1.089 (1.088)	2.253	114.72 (114.09)	128.95 (118.49)	110.49 (123.84)	0.0 (176.47)
6-311+G**	1.486 (1.481)	1.639 (1.641)	1.445 (1.456)	1.083 (1.082)	2.249	115.15 (114.82)	129.14 (117.99)	110.28 (119.13)	0.0 (176.34)
(B3LYP)									
6-311G**	1.506 (1.501)	1.645 (1.645)	1.439 (1.451)	1.087 (1.086)	2.247	113.84 (112.26)	129.71 (125.94)	110.81 (115.12)	0.0 (180.0)
(HF/6-31+G*)*	1.471 (1.469)	1.604 (1.604)	1.454 (1.458)						

Values in parenthesis refer to E-form.

(*) Nadia et al. Ref. [35] .

Table (21) : Total energy, net charges, bond orders and dipole moment of the isomers of sulfine (C_2H_3CHSO) at different levels and basis sets.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	H_9	S=O	C_3=S	C_3-C_4	O-H_9	
(RHF)											
6-31+G*	-588.21184 (-588.20572)	-0.73 (-0.71)	0.75 (0.77)	-0.34 (-0.36)	-0.13 (-0.11)	0.19 (0.21)	1.39 (1.42)	1.58 (1.63)	1.07 (1.01)		3.70 (4.49)
6-311+G*	-588.27567 (-588.26875)	-0.69 (-0.67)	0.74 (0.79)	-0.32 (-0.37)	-0.17 (-0.12)	0.16 (0.18)	1.37 (1.40)	1.58 (1.64)	1.05 (0.95)		3.77 (4.55)
6-311+G**	-588.30439 (-588.29874)	-0.71 (-0.70)	0.71 (0.72)	-0.08 (-0.06)	-0.17 (-0.10)	0.07 (0.03)	1.57 (1.62)	1.71 (1.76)	1.10 (1.02)		3.46 (1.08)
(MP2)											
6-31+G*	-588.93675 (-588.93145)	-0.55 (-0.54)	0.67 (0.67)	-0.38 (-0.37)	-0.05 (-0.07)	0.16 (0.18)	1.42 (1.45)	1.32 (1.33)	1.05 (0.99)		2.72 (3.11)
6-311+G*	-589.04834 (-589.04288)	-0.50 (-0.49)	0.68 (0.70)	-0.40 (-0.41)	-0.09 (-0.10)	0.15 (0.13)	1.42 (1.43)	1.32 (1.33)	1.04 (0.95)		2.67 (2.95)
6-311+G**	-589.12285 (-589.11678)	-0.51 (-0.51)	0.60 (0.59)	-0.15 (-0.12)	-0.11 (-0.09)	0.07 (0.04)	1.58 (1.62)	1.43 (1.46)	1.10 (1.00)	0.06	2.55 (2.88)
(B3LYP)											
6-311G**	-590.14051 (-590.13165)	-0.53 (-0.51)	0.61 (0.63)	-0.34 (-0.35)	-0.10 (-0.10)	0.15 (0.17)					3.20 (3.74)
(HF level)*	-588.21703										
(QCISD(T))*	-588.99146										

Values in parenthesis refer to E-form.

(*) Nadia et al. Ref. [35].

The π-conjugation is involved in both E- and Z-isomers, so the attractive electrostatic attraction between O...H is an effective factor for the over stability of isomer. The difference in energy between the two isomer is 5.56 kcal/mol using B3LYP/6-311G** level.

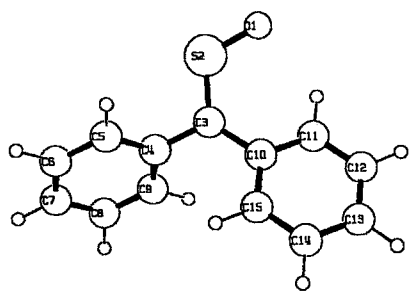
The ground state properties of the most stable Z- and E-conformers are given in table (20). The Z-isomer is completely planar while the vinyl group in E-form twisted by around 40° out of the CSO plane, which is reflected on elongation of the connecting C_3-C_4 bond in case of E-form and in same time decrease of its C=C bond length. This indicates a reduction in π-conjugation of E-form than Z-form. This is nicely reflected in the rotational barrier value, where it is 1.76 in case E-isomer and 0.68 in Z-one. The value of bond order of C-C is 1.10 and 1.02 for Z- and E-isomers, table (21).

The polarizability of the molecule depends on its charge distribution, so it is interesting to see the effect of introducing the C=C group (as an electron withdrawing group) on its polarizability. Table (21) depicteds the net charge on each atom of both isomers of thioacrolein S-oxide. The data reveal that in both isomers the pronounced effect of vinyl substitution is the withdrawing of the negative charge of carbon atom of sulfine group and its concentration on the directly connected carbon atom C_4. The charge on sulfur and oxygen atoms are not appreciably affected

by substituent, table (3,21). In other words, the polarizability of such molecule is reduced.

3.1.10. ARYL SULFINES

Aryl sulfines are subjected to extensive theoretical[26,81] and experimental[25]) investigation. The stability of aryl sulfinesshow that depending on the steric and electronic effect of aryl group.



E-phenyl Z-phenyl

In our work, the steric effect on sulfine structure is studied step wise of increasing substituent volume through study of the following compounds, viz: phenyl sulfine, methyl phenyl sulfine, o-, p- and m-methyl phenyl sulfine and diphenyl sulfine.

3.1.10.1. PHENYL SULFINE

The two stereoisomers of phenyl sulfine were fully optimized at RHF/6-31+G* level and B3LYP/6-311G** level and the results are given in tables (22,23).

Table (22) : Geometrical parameters of the two isomers of sulfine (PhCHSO) calculated at different levels and basis sets.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C_3=S	C_3-C_4	C_3-H_{15}	O-H_{11}	CSO	SC_3C_4	$H_{15}C_3S$	
(RHF)									
6-31G	1.705 (1.717)	1.673 (1.663)	1.434 (1.443)	1.075 (1.075)	2.084	110.02 (104.60)	131.42 (127.90)	112.13 (114.00)	0.13 (-0.39)
6-31+G*	1.470 (1.469)	1.603 (1.602)	1.459 (1.468)	1.078 (1.077)	2.279	115.57 (112.90)	132.12 (126.47)	110.49 (115.75)	0.18 (-0.75)
(MP2)									
6-31G	1.634 (1.623)	1.711 (1.710)	1.457 (1.465)	1.093 (1.092)	2.193	113.24 (110.08)	130.19 (125.08)	110.03 (114.24)	0.09 (-0.43)
(B3LYP)									
6-311G**	1.506 (1.503)	1.645 (1.645)	1.444 (1.452)	1.087 (1.086)	2.222	114.00 (112.24)	131.40 (125.92)	110.06 (115.24)	0.0 (180.0)

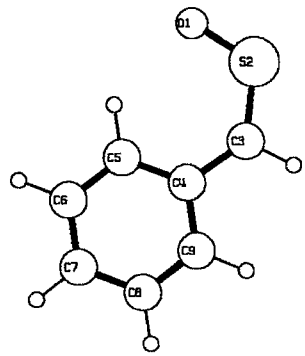
Values in parenthesis refer to E-form.

Table (23) : Total energy, net charges, bond orders and dipole moment of the two isomers of sulfine (PhCHSO) calculated at different levels basis sets.

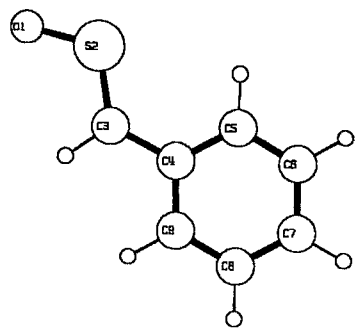
	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	H_{15}	S=O	C_3=S	C_3-C_4	C_3-H_{15}	
(RHF)											
6-31G	-740.66966 (-740.66391)	-0.77 (-0.75)	0.75 (0.74)	-0.49 (-0.48)	-0.05 (-0.02)	0.25 (0.28)	1.01 (0.99)	1.50 (1.55)	1.05 (0.97)	0.92 (0.90)	6.61 (8.46)
6-31+G*	-740.88594 (-740.87905)	-0.73 (-0.72)	0.74 (0.75)	-0.33 (-0.34)	-0.02 (0.002)	0.19 (0.21)	1.39 (1.40)	1.57 (1.59)	1.07 (1.02)	0.94 (0.93)	4.22 (5.34)
(MP2)											
6-31G	-741.47622 (-741.46981)	-0.67 (-0.66)	0.87 (0.88)	-0.59 (-0.59)	0.12 (0.13)	0.20 (0.22)	1.21 (1.24)	1.29 (1.29)	0.97 (0.92)	0.88 (0.88)	3.87 (4.85)
6-31+G*[a]	-742.12366 (-742.11690)	-0.73 (-0.72)	0.74 (0.75)	-0.33 (-0.40)	0.02 (0.04)	0.19 (0.27)	1.39 (1.40)	1.57 (1.60)	1.07 (1.02)	0.94 (0.90)	4.22 (5.35)
(B3LYP)											
6-311G**	-743.83371 (-743.82647)	-0.53 (-0.51)	0.61 (0.61)	-0.32 (-0.32)	-0.05 (-0.04)	0.15 (0.15)					3.64 (4.55)

Values in parenthesis refer to E-form.

[a] Single point calculations.



Z-form



E-form

The two isomers are coplanar and have nearly same bond lengths for CSO group while the C_3-C_4 bond is shorter in Z-form by 0.01 A°. The steric of the bulky phenyl group in case of Z-isomer is avoided by increasing the angle CSO or that between the ring and the sulfine group more than in case of the E-case. The interesting feature is bond length value of C_3-C_4 (bond connecting the CSO group and the ring) bond which is 1.459 and 1.468 A° for Z- and E-forms, respectively. The bond order values of this bond are 1.07 and 1.02, respectively. This means that it is a single bond contaminated with partial double bond character, conseq-uently the π-systems of both moieties are overlapped or extended. The π-system is more delocalized in case of Z-isomer (shorter bond and higher bond order); this leads to more stabilization for this isomer. The difference in energy between the two isomers is only 0.007 au or 4.32, 4.24, 4.54 kcal/mol at the levels of calculations.

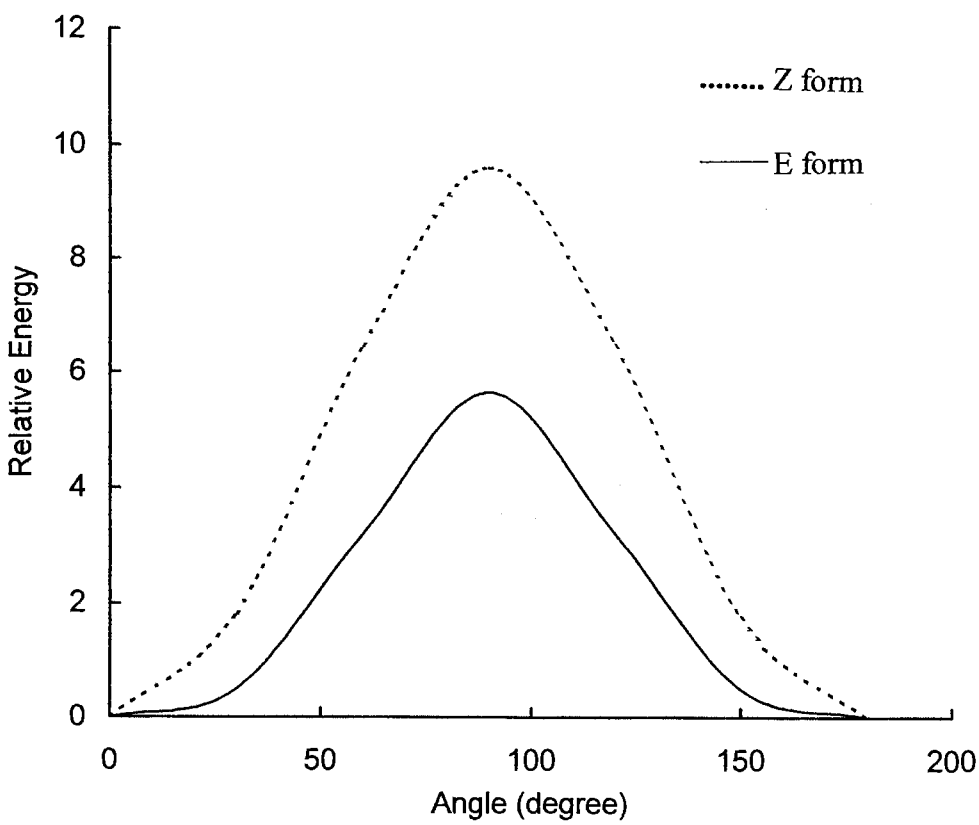


Fig. (2): Variation of total energy of Z- and E-phenyl sulfine with different dihedral angle calculated at MP2/6-31G* level.

Another factor for the stability of Z-conformer is the electrostatic attraction between the positive hydrogen H_{11} on the ring and the terminal negative oxygen atom.

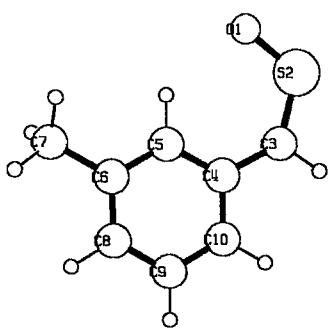
Figure (2) shows the rotation of the phenyl ring around connecting bond C_3-C_4, calculated at the same level of calculations. The rotational barrier is calculated to be 5.64 and 9.59 kcal/mol for the E- and Z-isomers, at MP2 level. The TS for this rotation is located at nearly perpendicular ring configuration.

The bond lengths of the molecules do not appreciably change during ring rotation. Except for the connecting bond C_3-C_4 which elongates and reaches its maximum value 1.482, 1.488 A° for Z- and E-isomers at the corresponding perpendicular form, i.e. it becomes more single bond and thus the π-conjugative extension overall the molecule is ruptured.

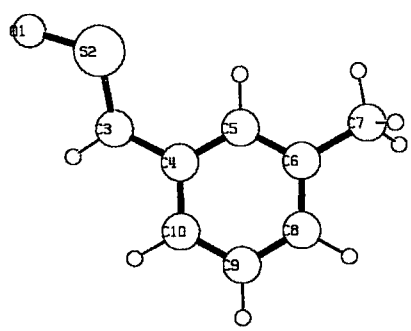
The calculated Mulliken atomic charges on different centers are given in table (23). The phenyl ring substitution decreases the negative charge on C_3 by about 0.16 with respect to the parent sulfine while the difference for O_1 and S_2 is only 0.05. Thus the CSO moiety becomes less polarized upon substitution.

3.1.10.2. META AND PARA METHYL PHENYL SULFINE

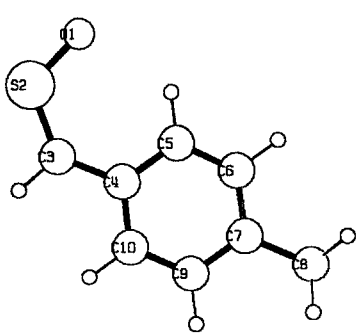
The optimized geometrical parameters of Z- and E-isomers of the titled compounds are depicted in tables (25,26). This data show that substitution with methyl group in meta or para position does not appreciably affect the relative stability between E- and Z-isomers and the ground state properties of both phenyl sulfine isomers.



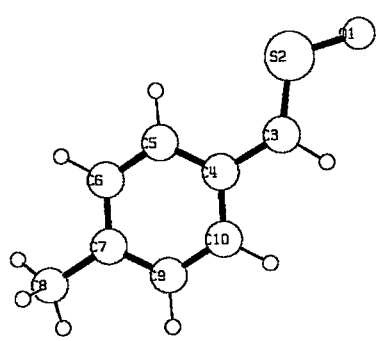
Z-form



E-form



Z-form



E-form

Table (24) : Total energy, net charges, bond orders and dipole moment of the two isomers of (m-methyl phenyl sulfine) calculated at different levels and basis sets.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	H_{18}	S=O	C=S	C_3-C_4	C_3-H_{18}	
(RHF)											
6-31G	-779.69126 (-779.68564)	-0.77 (-0.75)	0.75 (0.74)	-0.49 (-0.49)	-0.04 (-0.004)	0.25 (0.28)	1.01 (0.99)	1.50 (1.55)	1.04 (0.97)	0.92 (0.90)	6.35 (8.70)
6-31+G*	-779.92618 (-779.91968)	-0.73 (-0.72)	0.74 (0.75)	-0.33 (-0.34)	-0.01 (0.01)	0.19 (0.21)	1.39 (1.41)	1.57 (1.61)	1.06 (1.01)	0.94 (0.93)	3.99 (5.47)
(MP2)											
6-31G	-780.59306 (-780.58688)	-0.67 (-0.66)	0.86 (0.87)	-0.59 (-0.58)	0.12 (0.11)	0.20 (0.22)	1.20 (1.25)	1.29 (1.28)	0.97 (0.91)	0.88 (0.88)	3.61 (5.11)
6-31+G*[a]	-781.31127 (-781.30499)	-0.73 (-0.72)	0.74 (0.75)	-0.33 (-0.34)	-0.01 (0.01)	0.20 (0.21)	1.39 (1.41)	1.57 (1.61)	1.06 (1.01)	0.94 (0.93)	3.99 (5.47)

Values in parenthesis refer to E-form.

[a] Single point calculations.

Table (25) : Geometrical parameters of the two isomers of (m-methyl phenyl sulfine) calculated at different levels and basis sets.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C=S	C_3-C_4	C_3-H_{18}	O-H_{17}	CSO	C_4C_3S	$H_{18}C_3S$	
(RHF)									
6-31G	1.705 (1.717)	1.673 (1.663)	1.435 (1.444)	1.075 (1.075)	2.084	110.20 (104.61)	131.59 (127.94)	112.01 (113.98)	0.0 (180.0)
6-31+G*	1.471 (1.468)	1.603 (1.601)	1.459 (1.469)	1.078 (1.077)	2.274	115.69 (113.16)	132.29 (125.12)	110.36 (116.39)	0.0 (179.24)
(MP2)									
6-31G	1.635 (1.623)	1.712 (1.710)	1.456 (1.466)	1.093 (1.092)	2.184	113.26 (110.65)	130.27 (122.90)	109.96 (115.16)	0.0 (178.19)

Values in parenthesis refer to E-form.

Table (26) : Geometrical parameters of the two isomers of (p-methyl phenyl sulfine) calculated at different levels and basis sets.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C=S	C_3-C_4	C_3-H_{18}	O-H_{17}	CSO	C_4C_3S	$H_{18}C_3S$	
(RHF)									
6-31G	1.708 (1.720)	1.676 (1.666)	1.430 (1.439)	1.075 (1.075)	2.082	109.79 (104.43)	131.40 (128.01)	112.10 (113.91)	0.0 (180.0)
6-31+G*	1.472 (1.470)	1.604 (1.603)	1.457 (1.466)	1.078 (1.077)	2.280	115.45 (112.87)	132.06 (126.54)	110.53 (115.69)	0.0 (180.0)
(MP2)									
6-31G	1.636 (1.625)	1.710 (1.708)	1.456 (1.465)	1.093 (1.092)	2.192	113.14 (110.10)	130.15 (125.14)	110.15 (114.29)	0.0 (180.0)

Values in parenthesis refer to E-form.

Table (27) : Total energy, net charges, bond orders and dipole moment of the two isomers of (p-methyl phenyl sulfine) calculated at different levels and basis sets.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	H_{18}	S=O	C_3=S	C_3-C_4	C_3-H_{18}	
(RHF)											
6-31G	-779.69318 (-779.68720)	-0.77 (-0.75)	0.74 (0.72)	-0.49 (-0.48)	-0.06 (-0.03)	0.24 (0.28)	1.00 (0.98)	1.48 (1.54)	1.06 (0.98)	0.92 (0.90)	7.13 (9.32)
6-31+G*	-779.92703 (-779.91997)	-0.73 (-0.72)	0.73 (0.74)	-0.33 (-0.33)	-0.03 (-0.01)	0.19 (0.21)	1.39 (1.40)	1.57 (1.59)	1.07 (1.02)	0.94 (0.93)	4.52 (5.94)
(MP2)											
6-31G	-780.59237 (-780.58585)	-0.67 (-0.67)	0.86 (0.88)	-0.59 (-0.59)	0.12 (0.13)	0.20 (0.22)	1.20 (1.24)	1.30 (1.30)	0.98 (0.91)	0.88 (0.88)	4.10 (5.47)
6-31+G*[a]	-781.31113 (-781.30436)	-0.73 (-0.72)	0.73 (0.74)	-0.33 (-0.33)	-0.03 (-0.01)	0.19 (0.21)	1.39 (1.40)	1.57 (1.59)	1.07 (1.02)	0.94 (0.93)	4.52 (5.94)

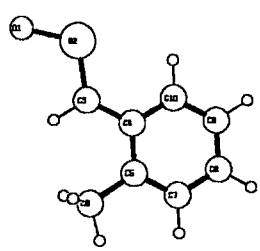
Values in parenthesis refer to E-form.

[a] Single point calculations.

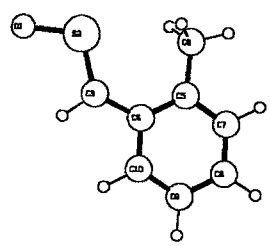
The bond length and bond angles are matched for the two isomers even O....H bond length. The above finding is also found in case of their atomic charges and bond order. Therefore, it is interesting that the Z-isomer is more stable than the E-isomer, in spite of probable steric interaction between oxygen atom and the bulky methyl phenyl group.

3.1.10.3. ORTHO METHYL PHENYL SULFINE

The bulky methyl group in ortho position will cause a remarkable steric effect on the geometry of sulfine molecule.

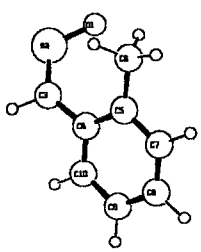


(A)

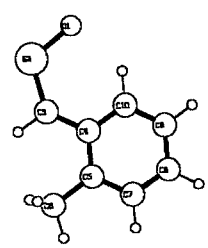


(B)

E-form



(C)



(D)

Z-form

The E-forms are completely planar and the two forms **A** and **B** are nearly of the same energy, table (28). The rotation of the aryl ring around C_3-C_4 is presented in figure (3). The highest energy conformer is the nearly perpendicular one which is 4.32 kcal/mol, at MP2 level, more than the corresponding planar one. That is due to the loss of π-conjugation upon twisting. Comparing to the geometry of phenyl sulfine (E-form), the geometrical parameters of the two molecules are nearly the same except for angles SC_3C_4 and $C_3C_4C_5$ which increase in the case of o-methyl derivative to avoid its sterric effect. The same result can be observed for the aquatically Mulliken atomic charges for the E-forms of the two compounds. Therefore, one can conclude that methyl substitution in ortho position in the case of E-conformations does not have any appreciable effect on the polarization or the geometry of the CSO moiety and thus its reactivity as 1,3-dipolar molecule or thiophlic reactions.

The molecular orbital calculations performed on the Z-conformer lead to two minima, one is planar while the other is twisted. The planar conformer which is the global minimum is that one where the methyl group is directed away opposite to the S=O bond. The other minimum correspond to a twisted conformer where the ring rotates 49° out of the CSO group. The rotation of aryl ring around the interlunar bond is depicted in figure (3).

Table (28): Ground states properties of different rotomers of o-methyl phenyl sulfine at MP2 level.

	T.E (Hartree)	Charges					Bond orders				Dm (Debye)
		O	S	C_3	C_4	H_{18}	S=O	C=S	C_3-C_4	C_3-H_{18}	
Z-form	-779.87905	-0.76	0.68	-0.31	-0.03	0.19	1.24	1.52	1.09	0.94	6.16
	(-779.89264)	(-0.77)	(0.68)	(-0.31)	(-0.05)	(0.20)	(1.22)	(1.53)	(1.11)	(0.94)	(6.18)
	[-779.91844]	[-0.72]	[0.76]	[-0.37]	[-0.01]	[0.19]	[1.42]	[1.61]	[0.99]	[0.93]	[3.79]
E-form	-779.88581	-0.77	0.69	-0.32	-0.03	0.23	1.23	1.55	1.05	0.93	7.48
	(-779.88706)	(-0.77)	(0.68)	(-0.31)	(-0.03)	(0.23)	(1.24)	(1.57)	(1.03)	(0.93)	(7.370

Values in parenthesis refer to dihedral angle=180 °

Values in two brackets refer to dihedral angle=49 °

Table (28) continue.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angle (Degree)
	S=O	C=S	C_3-C_4	C_3-H_{18}	O-H	CSO	SC_3C_4	SC_3H_{18}	
Z-form	1.626	1.719	1.468	1.096	2.063	118.53	140.05	104.56	4.06
	(1.633)	(1.713)	(1.459)	(1.090)	(2.158)	(113.92)	(130.42)	(108.91)	(4.15)
	[1.625]	[1.712]	[1.469]	[1.093]	[2.182]	[113.74]	[129.82]	[109.52]	[3.46]
E-form	1.625	1.715	1.464	1.094		108.60	129.98	111.52	5.03
	(1.623)	(1.710)	(1.467)	(1.090)		(109.83)	(124.99)	(113.32)	(4.69)

Values in parenthesis refer to dihedral angle=180 °
Values in two brackets refer to dihedral angle=49 °

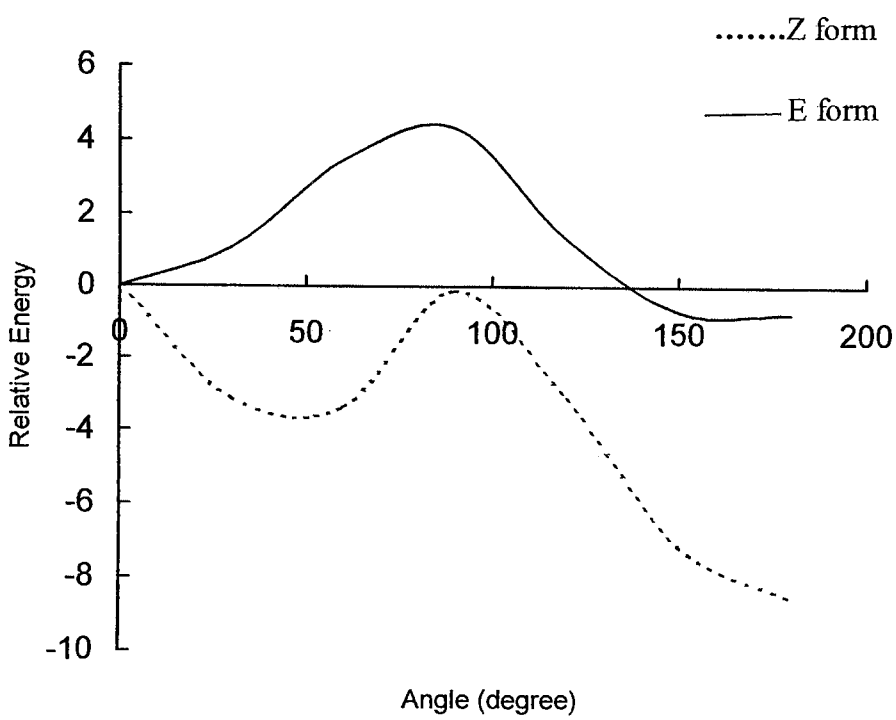
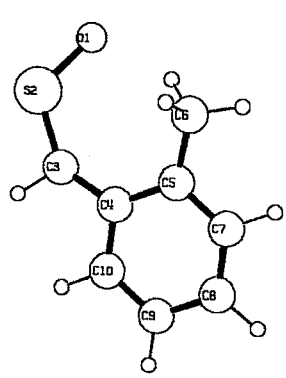


Fig. (3): Variation of total energy of Z- and E-o-methyl phenyl sulfine with different dihedral angle calculated at MP2/6-31G* level.

The figure shows that the difference in energy between the two minima is 1.82 kcal/mol at the MP2 level. The two minima are separated by a TS conformer which is twisted by 90° out of the plane and is higher by 5.14, 3.32 kcal/mol over the planar and twisted minima.

On the other hand, the other planar form which has a methyl group is alined the S=O bond corresponds to a maximum. Its energy is 7.15, 5.33 kcal/mol higher than the two minima. The main factors determining the relative stability of these conformers are the steric effect of methyl group, π-delocalization and electrostatic attraction. The global minima has a maximum π-delocalization, planar conformer, and electrostatic attraction, the charge on oxygen atom is -0.77 while that on hydrogen is 0.26 and less steric effect while the second minima has less π-delocalization due to twisting and electrostatic attraction. The steric effect of methyl group is the main factor of the unstability of the planar form (**E**) in spite of the existence of π-delocalization while the lack of π-delocalization in the case of the perpendicular conformer leads to its unstability. This is reflected on both of C_3-C_4 and O....H bond lengths, table (29).



(**E**) Z-form

It is interesting to compare between these different conformers with respect to their geometrical parameters. The difference in S-O and C-S bond lengths is negligible for Z- and E-forms, while in the case of Z-form the S-O bond length has its maximum at 180 °, 1.632 A ° at the perpendicular one, the reveres is found in case of the connecting bond C_3-C_4 bond. On the other hand, the C=S bond is not affected appreciably by the rotation. The main reason for such observation is the π-delocalization which reaches its maximum at the planar (180.0 °) and has minimum value at 90 ° conformer. The steric effect is reflected on the values of the CSO and CCS angles which have their maximum in the case of conformer **C**.

The Mulliken population analysis is given in table (30). All conformers of Z- and E-isomers have nearly the same atomic charges. Comparing to the atomic charges on CSO group of the parent phenyl sulfine, table (3) and (30), one notices that the introduction of methyl group on phenyl moiety does not affect these charges and its polarizability.

Table (29) : Geometrical parameters of the two isomers of (o-methyl phenyl sulfine) calculated at different levels and basis sets.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C=S	C_3-C_4	C_3-H_{18}	O-H_{16}	CSO	SC_3C_4	SC_3H_{18}	
(RHF)									
6-31G	1.693 (1.713)	1.666 (1.669)	1.447 (1.441)	1.075 (1.075)	2.066	111.55 (103.40)	133.04 (132.35)	111.02 (111.45)	40.90 (0.06)
6-31+G*	1.465 (1.470)	1.598 (1.608)	1.473 (1.466)	1.079 (1.078)	2.322	116.37 (111.50)	132.33 (131.81)	109.94 (112.54)	49.02 (0.11)
(MP2)									
6-31G	1.625 (1.625)	1.712 (1.715)	1.469 (1.464)	1.093 (1.094)	2.182	113.74 (108.60)	129.82 (129.99)	109.51 (111.51)	49.65 (0.06)

Values in parenthesis refer to E-form.

Table (30) : Total energy, net charges, bond orders and dipole moment of the two isomers of (o-methyl phenyl sulfine) calculated at different levels and basis sets.

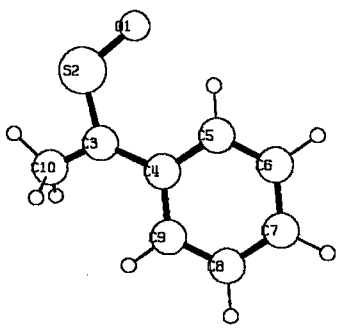
	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	H_{18}	S=O	C=S	C_3-C_4	C_3-H_{18}	
(RHF)											
6-31G	-779.67943 (-779.68246)	-0.76 (-0.77)	0.77 (0.75)	-0.47 (-0.49)	-0.05 (-0.04)	0.25 (0.28)	1.03 (0.98)	1.53 (1.51)	1.03 (1.01)	0.91 (0.90)	6.07 (8.50)
6-31+G*	-779.911844 (-779.91568)	-0.72 (-0.73)	0.76 (0.75)	-0.37 (-0.35)	-0.01 (-0.01)	0.19 (0.21)	1.42 (1.39)	1.61 (1.57)	0.99 (1.03)	0.93 (0.94)	3.79 (5.43)
(MP2)											
6-31G	-780.58813 (-780.58491)	-0.65 (-0.67)	0.86 (0.89)	-0.58 (-0.60)	0.08 (0.11)	0.21 (0.22)	1.24 (1.22)	1.26 (1.27)	0.93 (0.94)	0.87 (0.88)	3.46 (5.03)
6-31+G*	-781.30666 (-781.30335)	-0.72 (-0.73)	0.76 (0.75)	-0.37 (-0.35)	-0.01 (-0.01)	0.19 (0.21)	1.42 (1.39)	1.61 (1.57)	0.99 (1.03)	0.93 (0.94)	3.79 (5.43)

Values in parenthesis refer to E-form.

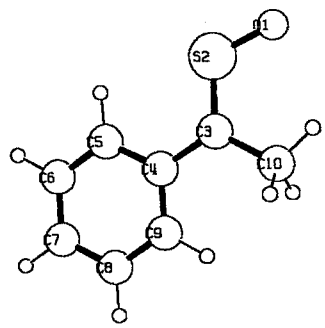
[a] Single point calculations.

3.1.10.4. METHYL PHENYL THIOKETON S-OXIDE

The computational results for this compound is given in tables (31,32) and presented below.



Z-form



E-form

The total energy of Z-conformer calculated at the RHF/6-31+G* level is –779.92358 au while that of E-one is –779.92100 au. Therefore, the Z-form is more stable by 1.62 kcal/mol. The two forms are planar, therefore they have the same π-delocalization which extended over the CSO and phenyl groups.

The π-conjugation over the CSO and phenyl groups stabilizes the two cases by the same extent. The Z-form is also stabilized by the electrostatic attraction between the terminal O_1 atom (charge = -0.75) and H (charge = 0.24) and the distance between these two atoms is 2.130 A °.

On the other hand, the two forms differ in C_3-C_4 (phenyl) and C_3-C_{10} (methyl) bond lengths where it is longer in the case of E-form by 0.015 A° for first bond and the reveres is found for second bond. This indicates more π-conjugation in the case of Z-form.

Table (31): Geometrical parameters of the two isomers of the sulfine (CH_3PhCSO) calculated at 6-31+G*

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angles (Degree)
	S=O	C=S	C_3-C_4	C_3-C_{10}	O-H	CSO	SC_3C_4	SC_3C_{10}	
(RHF)									
6-31+G*	1.474 (1.475)	1.616 (1.615)	1.474 (1.486)	1.514 (1.505)	2.130 (2.349)	116.54 (113.18)	127.94 (120.62)	112.40 (122.51)	0.14 (0.27)

Values in parenthesis refer to E-form.

Table (32): Total energy, net charges, bond orders and dipole moment of the two isomers of the sulfine (CH_3PhCSO) calculated at 6-31+G*.

	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	C_{10}	S=O	C=S	C_3-C_4	C_3-C_{10}	
(RHF)											
6-31+G*	-779.92358 (-779.92100)	-0.75 (-0.74)	0.72 (0.73)	-0.20 (-0.21)	-0.01 (0.01)	-0.04 (-0.4)	1.37 (1.37)	1.55 (1.57)	1.06 (1.02)	0.98 (0.96)	4.63 (5.26)
(MP2)											
6-31+G*[a]	-781.31029 (-781.30786)	-0.75 (-0.74)	0.72 (0.73)	-0.20 (-0.20)	0.01 (0.01)	-0.37 (-0.37)	1.37 (1.37)	1.55 (1.57)	1.06 (1.02)	0.98 (0.96)	4.63 (5.26)

Values in parenthesis refer to E-form.

[a] Single point calculations.

Comparing to phenyl sulfine results, table (22), one notices that the connecting bond C_3-C_4 elongates from 1.459 A° in the case of Z-phenyl sulfine to 1.475 A° at Z-form in our case at the same level of calculations, while the other bonds are nearly the same. This indicates less π-conjugation upon introduction of methyl group.

The electron releasing group (CH_3) accumulates the negative charge on the terminal oxygen atom in both isomers. The polarizability of C-S bond decreases compared to that of phenyl sulfine or its meta or para methyl derivatives.

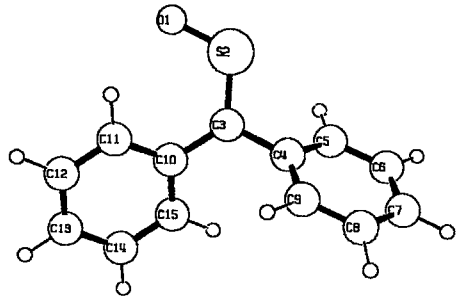
On the other hand, the O....H_{17} (E-form), calculated distance is 2.35 A ° , thus the strength of this attraction stabilizes the Z-form more than the corresponding E-form. Table (31) shows the ground state parameters for both isomers of the studied compound. The CSO angle increases in Z-case by about 3 ° to avoid the phenyl ring steric. The different bond lengths of the two isomers are the same except of bonds C_3-C_4 and C_3-C_{10} which connect the CSO group with the phenyl and methyl groups, respectively. The first bond is shorter in both isomers due to extension of π-electron over the CSO and phenyl groups.

3.1.10.5. DIPHENYL SULFINES

The NMR spectra of 4,4̀-disubstituted diphenyl sulfines were measured and discussed in terms of the deshielding effect of the CSO

group on the ortho- and meta-protons of either phenyl ring[23]. The data reveal that the deshielding effect of CSO group is directed to one side of molecule and the deshieding effect on ortho protons depends on the type of ring substituent.

Owing to the high molecular weight of diphenyl sulfine and the no. of 3N-6 variables, the RHF/6-31G* level was used for its optimization. The ground state energy and properties were improved by MP2 single point energy. The calculations shows that the Z-ring rotate of the plane by angle -28.2 ° while the E-one rotate of plane by 52.8 ° . This means that the two rings have different π-electron interaction extent with the sulfine group, which is shown in the C_3-C_x distance, where it is shorter in case of Z-ring by 0.015 A° . In previous work[81] the result obtained (the Z-phenyl ring twisted by only 25 ° from the plane, while the E-phenyl ring twisted by 50 °). On the other hand, the Z-ring is stabilizes by electrostatic attraction O....H. It is interesting to compare between the geometry of Z-ring and that of Z-phenyl sulfine. The C_3-C_x is shorter in case of Z-phenyl sulfine which means more delocalization. The C=S and S=O bond lengths are shorter in case of Z-phenyl sulfine. While in the E-ring the C_3-C_X bond is longer than the E-phenyl sulfine. Also, the C=S and S=O bond lengths are shorter in case of E-phenyl sulfine.



Z-ring E-ring

Table (33): Geometrical parameters of (Diphenyl sulfine) calculated at different basis sets.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angle (Degree)
	S=O	C=S	C_3-C_4	C_3-C_{10}	O-H	CSO	SC_3C_4	SC_3C_{10}	
(RHF)									
6-31G	1.706	1.698	1.480	1.457	2.108	110.91	114.55	125.42	-46.88
6-31G*	1.472	1.6178	1.493	1.478	2.328	115.39	113.98	121.33	-52.75

Table (34): Total energy, net charges, bond orders and dipole moment of diphenyl sulfine calculated at different levels and basis sets.

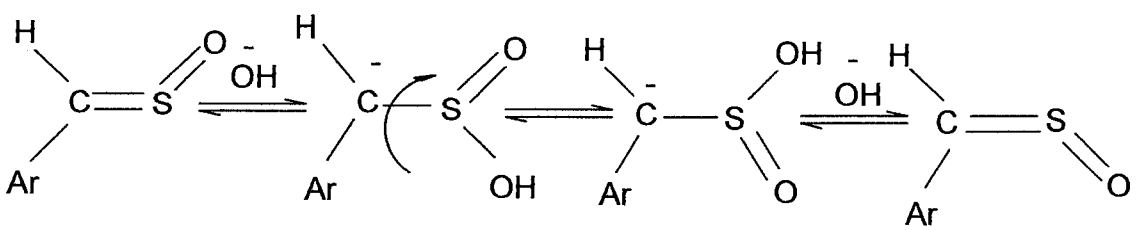
	T.E (Hartree)	Charges					Bond orders				Dipole moment (Debye)
		O	S	C_3	C_4	C_{10}	S=O	C=S	C_3-C_4	C_3-C_{10}	
(RHF)											
6-31G	-970.13882	-0.77	0.75	-0.34	-0.08	-0.06	1.00	1.47	0.99	1.03	7.66
6-31G*	-970.42061	-0.73	0.75	-0.22	-0.02	0.01	1.38	1.57	0.98	1.02	5.00
(MP2)											
6-31G[a]	-971.43638	-0.85	0.93	-0.39	-0.06	-0.04	1.04	1.41	0.98	1.01	6.26
6-31G*[a]	-972.38635	-0.73	0.75	-0.22	-0.02	0.01	1.38	1.57	0.98	1.02	4.99

[a] Single point calculations.

3.2. (E)-(Z) INTERCONVERSION

The E- and Z-isomers are experimentally produced in different ratios depending on type of substituent, reaction conditions and steric hindrance. It was found that the E-isomers is kinetically controlled product while the Z-one is thermodynamically controlled product[10]. S. Watamabe et al.[10] found that E-isomer of t-butyl phenyl sulfine which is produced as a major product is a stable with regard to thermal isomerization i.e. it does not change into Z-form even after refluxing, while in the presence of a base it undergoes a facile isomerization, which means that Z-isomer is thermodynamically more stable than E-one.

On the other hand, W. J. Noble et al.[11] studied the rearrangement of allyl vinyl sulfoxide into the corresponding sulfine. The E-form was the predominant one as a kinetically controlled product. The Z-isomer is produced very slowly as an E- to Z-isomerization process.



(E) (Z)

The above mechanism reveal that the isomerization process depends on the rotation of S=O group around C-S bond. This rotation will easily undergo when the C-S bond possesses a more single bond

character. Therefore, any substituent that increases the polarization of C-S bond will help the isomerization process.

To our knowledge, the only E- to Z-sulfine isomerization was theoretically studied[27] early using ab initio and INDO procedures for the parent sulfine. Two paths were studied; inversion path with the oxygen atom remaining in the molecular plane and the other path is the rotation around the C-S bond. The results were poor with respect to the experimental values due to small basis set used and the limited optimization. The inversion experimental barrier value is 18.0 kcal/mol while that for the rotation is 23 kcal/mol[79]. The calculated barrier overestimated the experimental ones. The difference diminishes upon adding number of d-function on the S atom.

In this part, the isomerization process through the rotation around the C-S bond is studied theoretically using B3LYP/6-311G** level. Full optimization for both the ground states (E- and Z-) and the transition state was performed and the nature of the latter point was confirmed by vibration frequency calculations, imaginary one. Different substituted sulfines will be studied in gas phase to elucidate the substituent effect on the isomerization.

Table (35) shows the geometrical parameters of both isomers E- and Z- of parent sulfine and its substituted compounds and their detected transition states. Comparing the bond lengths of the two states of H_2CSO

molecule shows that both of S-O and C-S bonds elongate in transition state by 0.15 A ° and 0.06 A ° , respectively. The oxygen atom rotates by angle 63.5 ° out of the molecule plane so the CSO angles decrease from 114.7 ° in ground state to 76.5 ° in TS. The elongation of these bonds indicates their increase in their single bond character in TS. Table (36) shows the atomic charges on different atoms in both states. The polarization decreases in case of transition state.

The total energy of the rotated transition state is -512.6299 au while that of the stable molecule is -512.7188 au at B3LYP/6-311G**. The activation energy, $\Delta E = E_S - E_{TS}$ is 55.74 kcal/mol which is still larger than the experimental value 23 kcal/mol. This means that in spite of a large basis set used, the level failed to obtain reliable activation energy value in our case.

The results for ethanethial S-oxide are depicted in table (35). As in case of the parent, the C-S and S-O bonds elongate upon rotation while the C-C bond becomes more shorter by about 0.02 A °. The angle of rotation of oxygen atom is around 66.4 ° . The electrostatic attraction between the terminal oxygen atom and the methyl hydrogen atom decreases in spite of increase of positive charge on the latter due to orientation of oxygen atom toward sulfinic hydrogen. This is reflected on the increases of the O....H distance from 2.568 A ° at Z-isomer to 4.006 A ° at the transition state.

Energetically, the transition state of ethanethial S-oxide is higher than the Z- and E-states by 47.95 and 45.15 kcal/mol, respectively. The decrease in activation energy between that of the parent and of ethanethial S-oxide is attributed to the stability of transition state of the latter due to electrostatic attraction with sulfinic hydrogen.

The isomerization of Z- to E-flourosulfine derivative was calculated and the results are given in table (35) and figure (6). The bond lengths and bond angles of the obtained transition state are nearer to the E-form values and thus the distance O...H decreases to 2.241 A °. The dihedral angle of oxygen atom is 59.3 ° . The activation energies of isomerization are 36.25 and 36.78 kcal/mol for E- to Z-isomerization and Z- to E-isomerization, respectively. The same results are obtained for chlorosulfine isomerization table (35) and figure (7). The geometrical parameters of CSO group are nearly the same for the two compounds. The activation energy for the chloro-derivative is higher by about 5 kcal/mol. This means that as the electronegativity of the substituent increases, the isomerization process becomes much easier.

Figure (8) shows the relative energies of both of E- and Z-aldehyde sulfine and their interconversion transition state. The figure shows that the Z- to E-isomerization process through a barrier of 51.8 kcal/mol while the E- to Z-one needs only passes 50.8 kcal/mol. This high value relative to the hydrogen derivative is due to the high stability of Z- and E-forms

of aldehydic isomer by a π-delocalization and electrostatic interaction between the terminal oxygen and aldehydic hydrogen atom. This is reflected in the elongation of C_3-C_4 bond in transition state relative to that of Z-form while the CSO parameters are closer to those of chloride form.

The E- to Z-form of amino derivative isomerization passes through an activation barrier of 27.47 kcal/mol, the reverse process need a higher energy, 36.61 kcal/mol. Table (35) shows the geometrical parameters of transition state, which has a largest CSO group bond lengths of the studied compounds. It is also interesting to note that the transition state is geometrically closer to the Z-isomer, the O....H_5 distance is 2.30 A ° , therefore, as in case of ethanethial S-oxide this electrostatic attraction stabilizes the TS and thus decreasing the activation energy.

The less value of amino activation barrier in spite of the stability of Z-form is also due to the longer bond length C-S (1.668 A ° in Z-form to 1.709 A ° in TS) which means a more single bond character, so facilitator the rotation of S-O bond around C-S bond.

Table (35) : Geometrical parameters of three conformers; E, Z and corresponding TS of FCHSO, CH_3CHSO, NH_2CHSO, CHOCHSO, ClCHSO and H_2CSO calculated at 6-311G**/B3LYP.

	Bond lengths (Angstrom)					Bond angles (Degree)			Twist angle (Degree)
	S=O	C=S	C-**X**	C-H	O-H	CSO	CS**X**	CSH	
FCHSO	1.497 (1.501) [1.649]	1.639 (1.642) [1.673]	1.325 (1.335) [1.317]	1.086 (1.085) [1.082]	 [2.241]	114.32 (111.35) [76.84]	124.31 (118.80) [124.38]	119.42 (124.94) [120.69]	0.0 (180.0) [86.57]
CH_3CHSO	1.501 (1.498) [1.644]	1.631 (1.630) [1.694]	1.489 (1.496) [1.479]	1.086 (1.087) [1.083]	2.568 [2.207]	113.50 (114.30) [77.11]	125.08 (121.17) [125.77]	113.24 (118.11) [113.10]	0.0 (180.0) [85.23]
NH_2CHSO	1.536 (1.519) [1.651]	1.668 (1.665) [1.709]	1.339 (1.357) [1.327]	1.083 (1.086) [1.083]	2.167 [2.300]	105.43 (110.97) [78.82]	118.18 (125.87) [126.02]	120.76 (116.86) [115.68]	0.0 (180.0) [86.28]
CHOCHSO	1.492 (1.490) [1.640]	1.638 (1.637) [1.699]	1.470 (1.470) [1.477]	1.086 (1.085) [1.082]	2.689 [2.244]	113.93 (116.23) [74.97]	125.79 (127.81) [124.45]	114.86 (116.92) [116.64]	0.0 (180.0) [88.76]
ClCHSO	1.491 (1.496) [1.647]	1.638 (1.640) [1.678]	1.712 (1.727) [1.718]	1.083 (1.083) [1.079]	 [2.238]	114.51 (111.91) [76.00]	125.59 (121.11) [118.59]	116.97 (121.98) [126.55]	0.0 (180.0) [86.93]
H_2CSO	1.496 [1.643]	1.620 [1.683]	1.083 [1.081]	1.083 [1.086]		114.48 [76.49]	116.14 [115.79]	122.90 [123.97]	0.0 [86.40]

Values in parenthesis refer to E-form.
Values in two brackets refer to TS.

Table (36) : Total energy, net charges and dipole moment of three conformers; E, Z and corresponding TS of FCHSO, CH_3CHSO, NH_2CHSO, CHOCHSO, ClCHSO and H_2CSO calculated at 6-311G**/B3LYP.

	T.E (Hartree)	Charges					Dipole moment (Debye)	ΔE (kcal/mol)
		O	S	C	X	H		
FCHSO	-611.95904 (-611.95824) [-611.90038]	-0.52 (-0.53) [-0.54]	0.59 (0.62) [0.44]	-0.07 (-0.08) [-0.04]	-0.15 (-0.16) [-0.12]	0.15 (0.16) [0.18]	3.79 (2.21) [2.65]	0.0 (0.50) [36.78]
CH_3CHSO	-552.04616 (-552.04170) [-551.96969]	-0.54 (-0.53) [-0.53]	0.63 (0.62) [0.41]	-0.39 (-0.37) [-0.24]	-0.28 (-0.28) [-0.27]	0.16 (0.17) [0.19]	3.59 (4.05) [3.73]	0.0 (2.79) [47.95]
NH_2CHSO	-568.09932 (-568.08474) [-568.04093]	-0.62 (-0.58) [-0.60]	0.52 (0.52) [0.34]	-0.15 (-0.17) [-0.07]	-0.39 (-0.41) [-0.34]	0.14 (0.16) [0.17]	4.94 (6.38) [6.01]	0.0 (9.14) [36.61]
CHOCHSO	-626.06326 (-626.06165) [-625.98060]	-0.49 (-0.47) [-0.46]	0.69 (-0.68) [0.46]	-0.41 (-0.38) [-0.25]	0.20 (0.18) [0.20]	0.18 (0.16) [0.20]	2.54 (3.52) [2.72]	0.0 (1.01) [51.83]
ClCHSO	-972.32936 (-972.32517) [-972.25916]	-0.50 (-0.51) [-0.51]	0.67 (0.69) [0.49]	-0.41 (-0.41) [-0.27]	0.04 (0.02) [0.06]	0.20 (0.21) [0.23]	3.34 (2.14) [2.53]	0.0 (2.62) [44.01]
H_2CSO	-512.71885 [-512.62999]	-0.44 [-0.50]	0.51 [0.43]	-0.43 [-0.29]	0.22 [0.19]	0.13 [0.16]	3.47 [2.96]	0.0 [55.71]

Values in parenthesis refer to E-form.
Values in two brackets refer to TS.

Table (37) : Thermodynamic energies parameters of TS for H_2CSO, FCHSO, CH_3CHSO, CHOCHSO, NH_2CHSO and ClCHSO.

	H_2CSO	FCHSO	CH_3CHSO	CHOCHSO	NH_2CHSO	ClCHSO
Imaginary Frequencies	-740.6529	-475.2612	-547.5605	-655.0286	-334.5543	-515.8212
Zero-point correction	0.027693	0.020677	0.055574	0.03718	0.046120	0.019079
Thermal correction to energy	0.030862	0.024359	0.060174	0.042223	0.050306	0.023075
Thermal correction to enthalpy	0.031806	0.025303	0.061119	0.043167	0.051250	0.024020
Thermal correction to Gibbs free energy	0.002462	-0.006158	0.027994	0.008262	0.019099	-0.008781
Sum of electronic and zero-point energies	-512.60230	-611.87970	-551.91411	-625.97338	-567.99481	-972.24008
Sum of electronic and thermal energies	-512.59913	-611.87602	-551.90951	-625.93838	-567.99062	-972.23608
Sum of electronic and thermal enthalpies	-512.59819	-611.87507	-551.90856	-625.93744	-567.98968	-972.23514
Sum of electronic and free energies	-512.62753	-611.90654	-551.94169	-625.97234	-568.02183	-972.26794

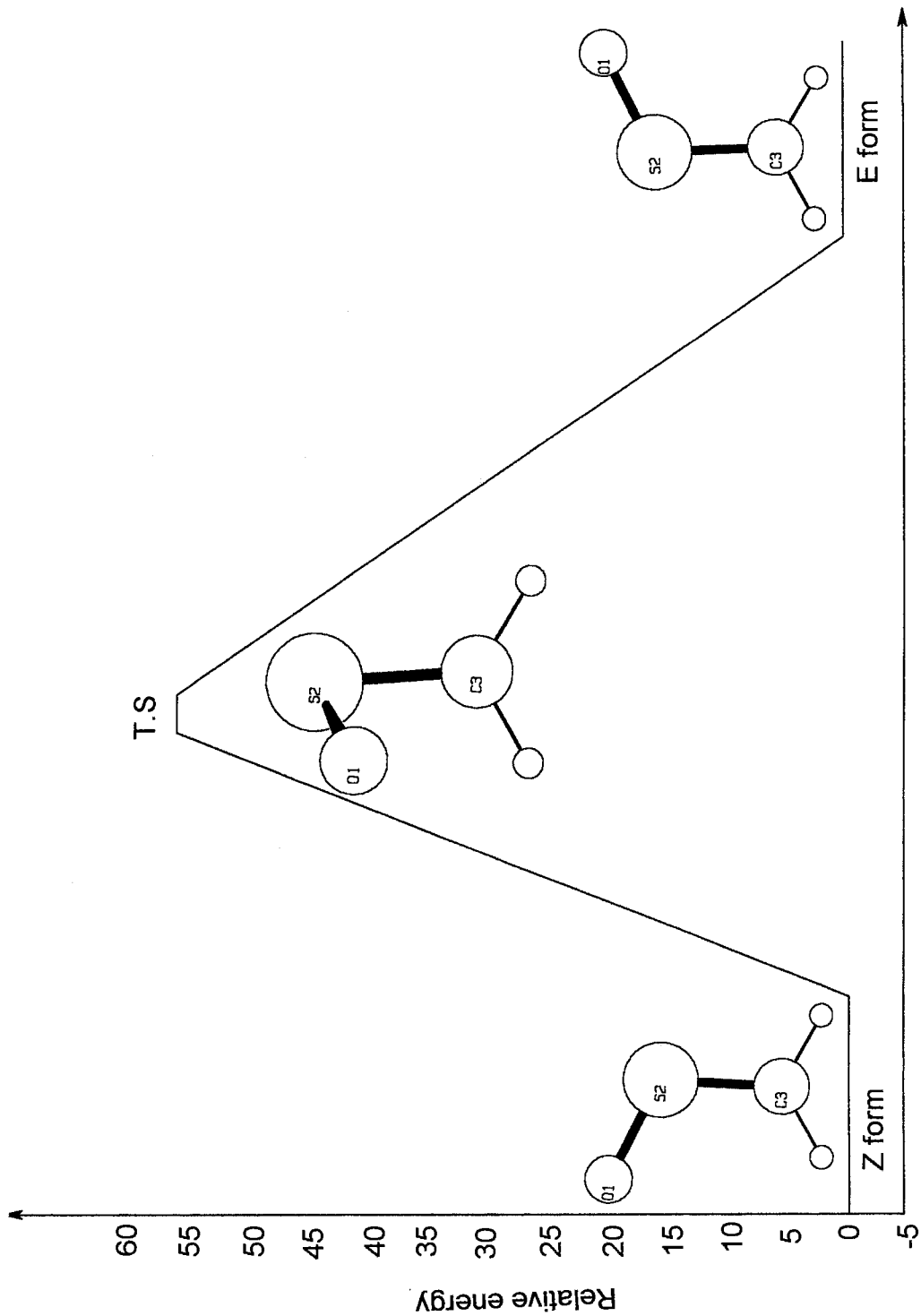


Fig. (4): Relative energy of different conformers of (H_2CSO) calculated at the B3LYP/6-311G**.

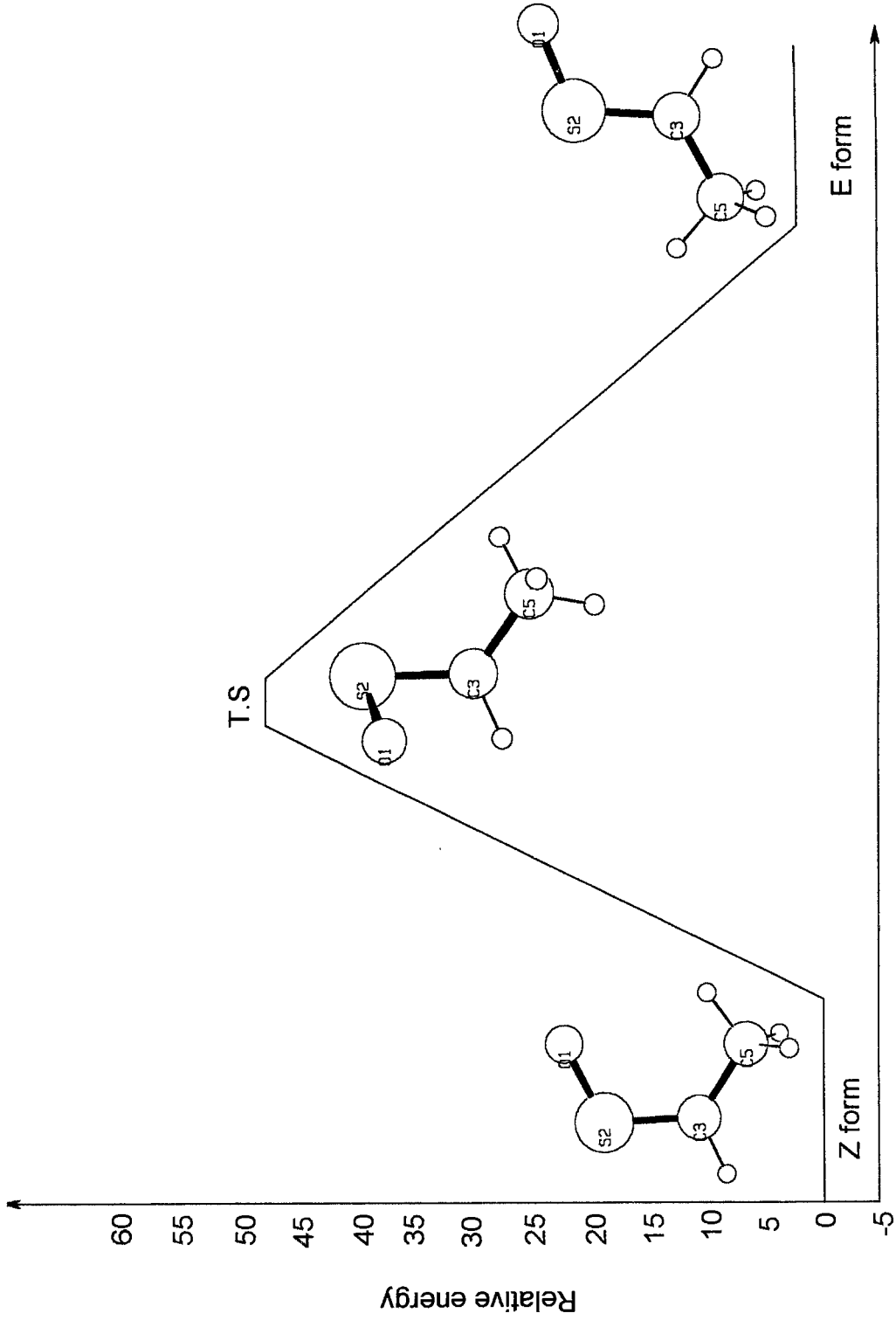


Fig. (5): Relative energy of different conformers of (CH_3CHSO) calculated at the B3LYP/6-311G**.

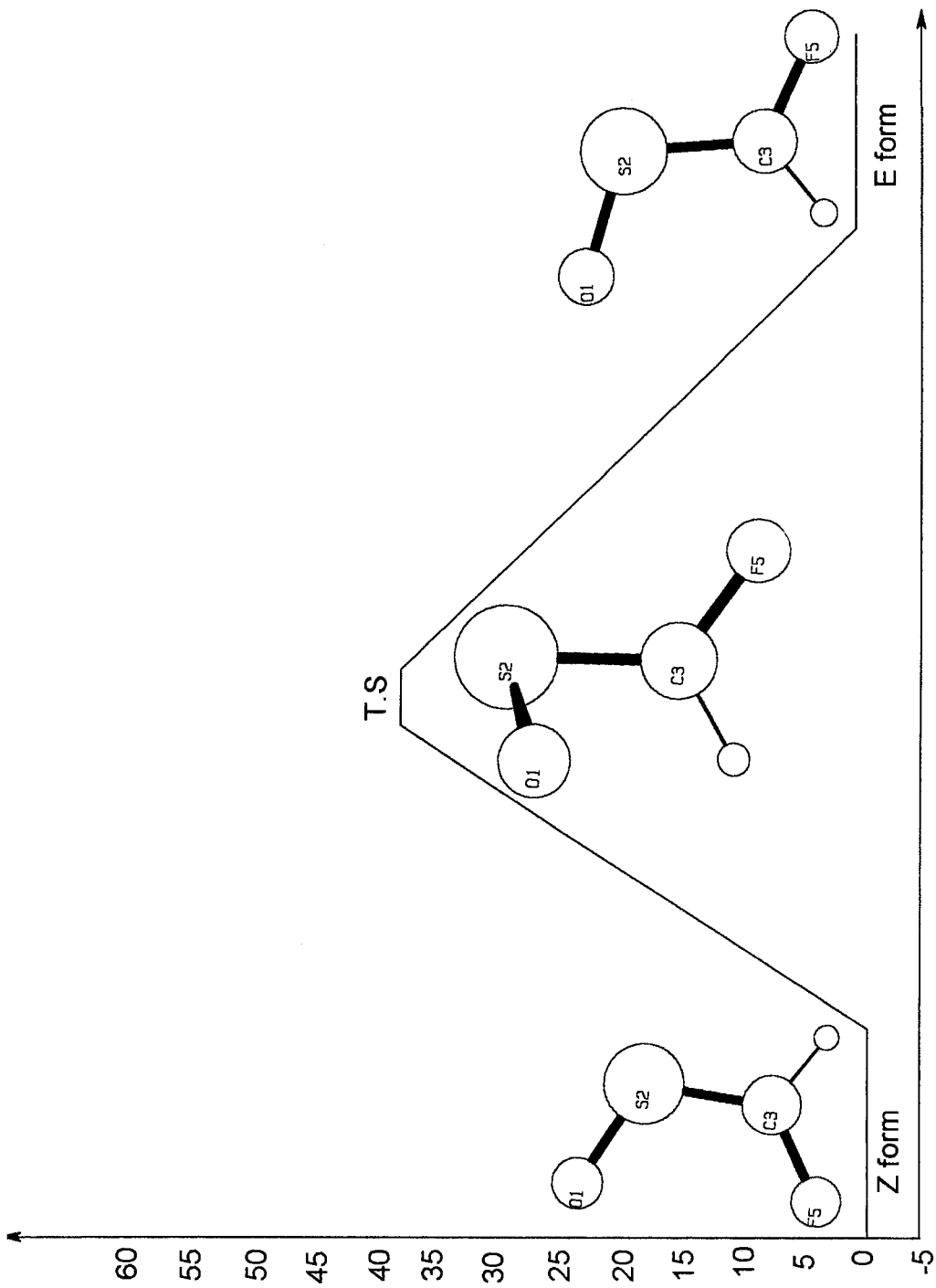


Fig. (6): Relative energy of different conformers of (FCHSO) calculated at the B3LYP/6-311G**.

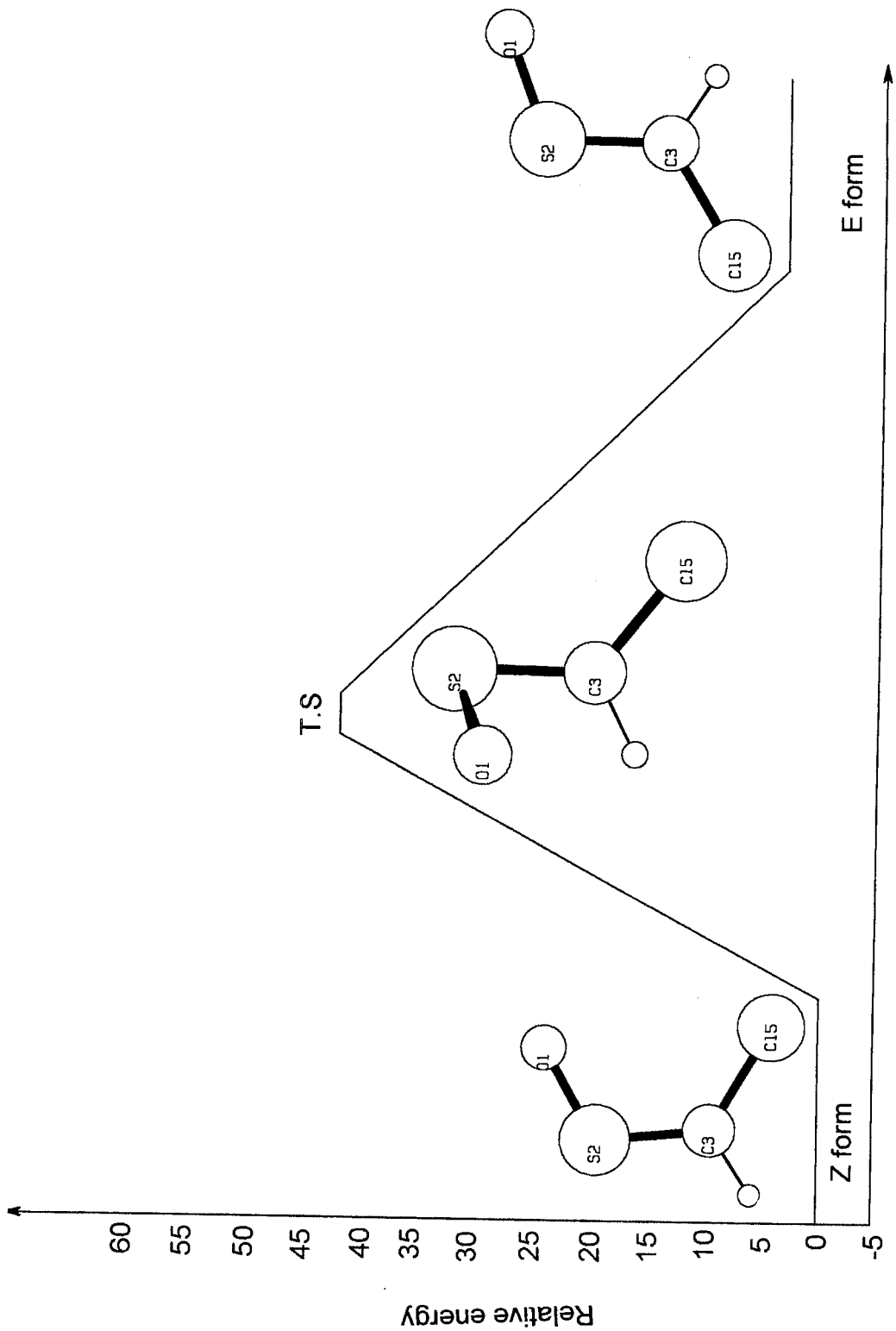


Fig. (7): Relative energy of different conformers of (ClCHSO) calculated at the B3LYP/6-311G**.

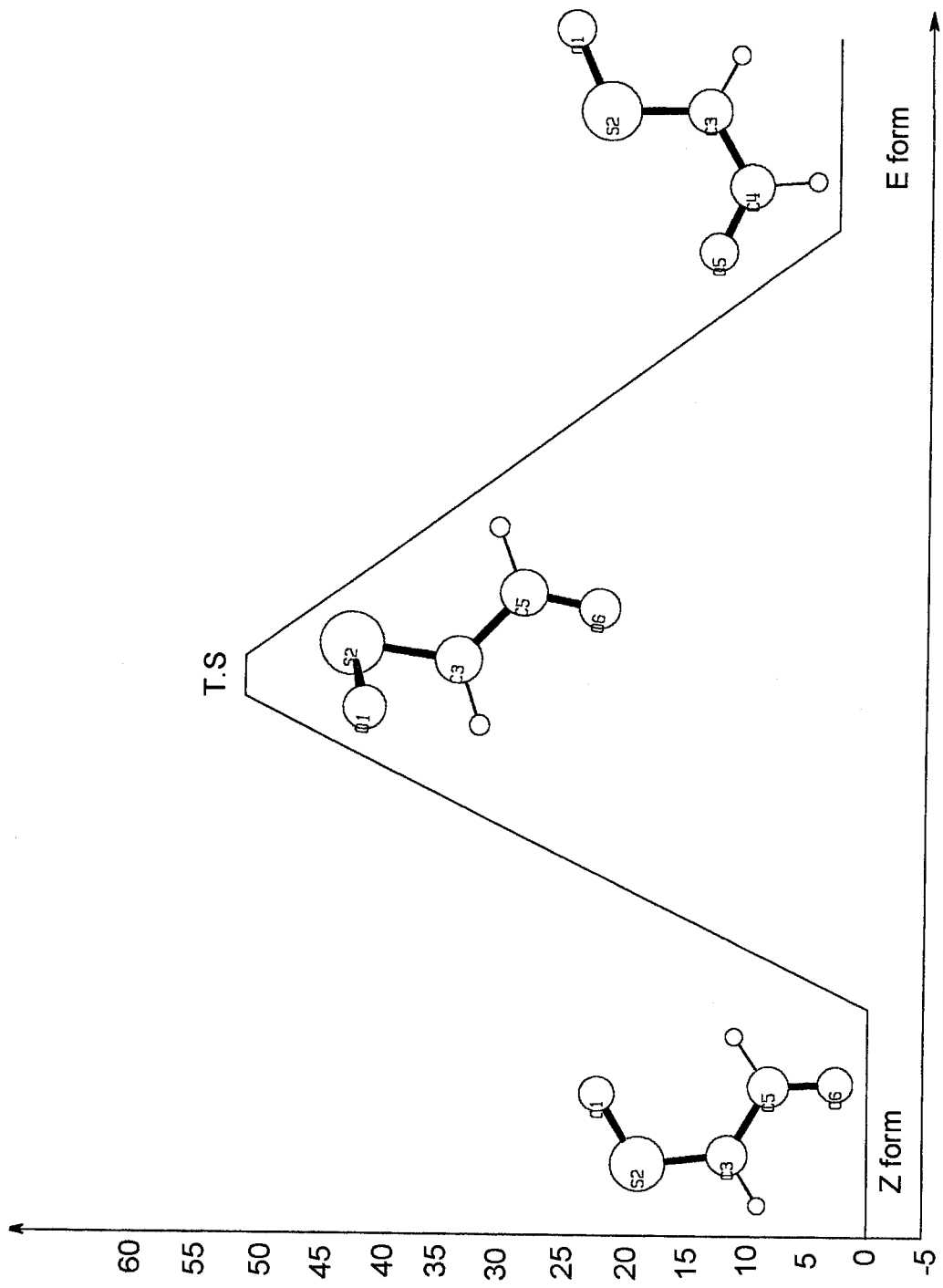


Fig. (8): Relative energy of different conformers of (COHCHSO) calculated at the B3LYP/6-311G**.

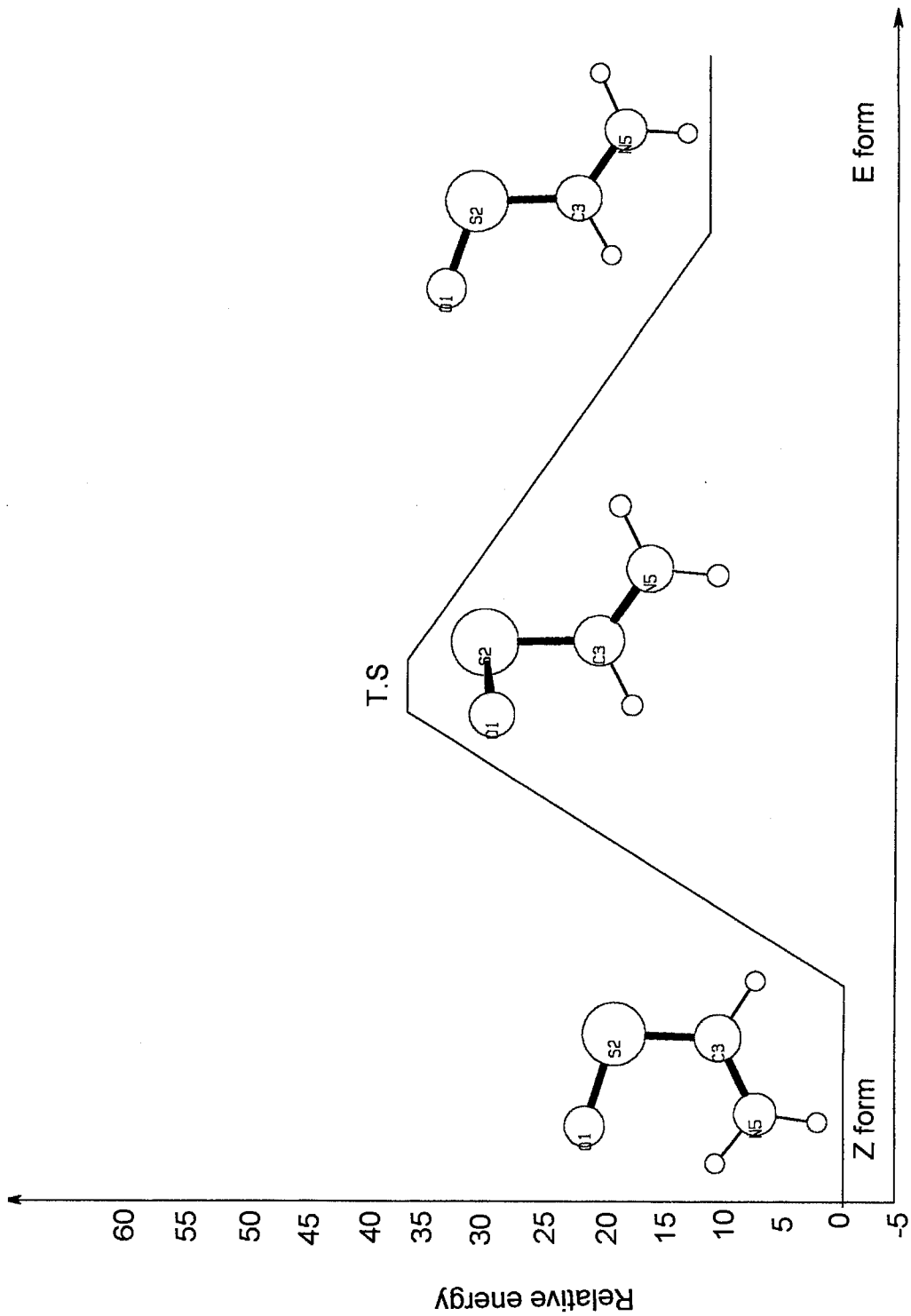


Fig. (9): Relative energy of different conformers of (NH_2ChSO) calculated at the B3LYP/6-311G**.

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