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Molecular Orbital Calculations on the Ethylene Episulfide Molecule and Its Isomers

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Systematic non-empirical and semi-empirical molecular orbital studies have been performed on the sulfur atom + ethylene system and its reaction products thiirane and vinylmercaptan. The results are in general agreement with earlier qualitative and semiquantitative rationalizations of the reaction but also bring to light a number of novel features.

Es wurden systematische nichtempirische und semi-empirische MO-Rechnungen am System Schwefelatom und Äthylen und seinen Reaktionsprodukten Thiiran und Vinylmercaptan durchgeführt. Obwohl die Resultate im allgemeinen mit früheren qualitativen und semiquantitativen Erkenntnissen übereinstimmen, zeigen sie doch eine Anzahl neuer Gesichtspunkte.

Introduction

The experimental observation [1, 2] that ground triplet state sulfur atoms add across olefinic bonds to yield thiirane in a concerted, stereospecific manner has generated considerable interest [3, 4] in the theoretical interpretation of this reaction, because it is the first example of a stereospecific cycloaddition of a divalent triplet state reagent.

A recent theoretical study of the interaction of sulfur atoms with ethylene within the framework of the Extended Hückel Molecular Orbital (EHMO) theory has been reported by Hoffmann and coworkers [4]. Potential surface calculations revealed the presence of two minima for the $S(^1D_2) + C_2H_4$ system. The higher of these corresponds to vinyl mercaptan formation *via* C–H bond insertion, and the lower minimum, lying about 20 kcal/mole below the former, to the symmetry-allowed, least-motion, addition of sulfur across the double bond. The two are viewed as competing concerted processes. Similar calculations for the $S(^3P)$ configuration indicated the presence of only one minimum in the potential surface, leading to thiirane formation. The stereospecificity of the addition reaction was attributed to a correlation with an excited state of thiirane which retains C–C bonding but is unstable with respect to C–S ring opening. The ring-opened thiirane intermediate has a CCS bond angle of 110° and the plane of the terminal methylene group is perpendicular to the CCS plane. The calculated energy barrier for rotation of the methylene was 5 kcal/mole.

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Two Hartree-Fock type MO calculations on the thiirane molecule also appeared in the past two years [5, 6]. These were concerned only with the electronic structure of the molecule in its most stable conformation.

The present study was undertaken in order to re-examine the addition reaction and elucidate the molecular structure of the various isomeric C_2H_4S product molecules, thiirane, vinylmercaptan and thioacetaldehyde, using both *ab initio* and semiempirical MO methods. In this article we report the structural results of these studies, while details of the reaction surface will be discussed in a subsequent communication [7].

Method

Accurate molecular Hartree-Fock (HF) calculations on sulfur compounds are very much in their infancies compared to the accumulated theoretical knowledge of oxygen and nitrogen containing organic compounds [8–11]. It is relatively easy to perform conformational studies on organic sulfur compounds [12, 13], just as well as on any other compounds containing heteroatoms [14–16]. However, the study of reactions involving bond making and/or breaking processes is an order of magnitude more difficult problem, even in the thermodynamic sense

Table 1. The breakdown of total energy to experimental and theoretical components for thiirane and its constituent atoms

A) Data for the constituent atoms of C_2H_4S:

Atom	E_{HF}[a]	E_{corr}[b]	E_{rel}[c]	Sum for C_2H_4S
C	− 37.6886	−0.1581	−0.0130	− 75.7194
S	−397.5047	−0.6400	−1.0510	−399.1957
H	− 0.5000	—	—	− 2.0000
Sum for C_2H_4S	−474.8819	−0.9562	−1.077	−476.9151

[a] Ref. [20]; [b] Ref. [21]; [c] Ref. [22].

B) Data for thiirane:

Experimental components	E (hartree)	Theoretical component	E (hartree)
Total atomic energy	−476.915[a]	Hartree-Fock energy[f]	−475.640
Total bond energy	− 0.948[b]	Correlation energy[e]	− 1.199
Zero-point energy	− 0.053[c]	Relativistic energy[d]	− 1.077
Experimental energy	−477.916	Total energy	−477.916

[a] Given as the final sum in Table 1A.

[b] Calculated from heats of formation [23, 24].

[c] Calculated as $E_{ZPV} = \frac{1}{2}hc \sum_{i=1}^{15} \tilde{\nu}_i$ where $\tilde{\nu}_i$ are the fifteen fundamental vibrations (in units of cm^{-1}) as taken from Ref. [24]. A more recent vibrational study uses similar frequencies [25].

[d] Assumed to be equal to that of the atomic relativistic energy (E_{rel}) in Table 1A.

[e] The molecular correlation energy of C_2H_4S was calculated as the following sum: $E_{corr}(CH_2{=}CH_2) + E_{corr}(S) + \Delta E_{corr}(\text{bond}) = 0.534 - 0.640 - 0.065 = -1.199$ hartree.

[f] The Hartree-Fock Limit (HFL) was estimated as $E_{HF} = E_{exp} - (E_{corr} + E_{rel})$.

[17–19]. This is apparent from the data in Table 1. The difference between the molecular and atomic Hartree-Fock Limits (HFL) gives a relatively small binding energy,

$$E_{\mathrm{HFL}}^{\mathrm{molec}} - E_{\mathrm{HFL}}^{\mathrm{atoms}} = -475.640 + 474.882 = -0.758 \text{ hartree},$$

as compared to the experimental dissociation energy (−0.948 hartree). This discrepancy (approximately 0.19 hartree) in the total dissociation (i.e. atomization) corresponds to ca. 120 kcal/mole. Fortunately, as it will be discussed later, the dissociation energy of thiirane to ethylene and sulfur atom carries a considerably smaller error in the Hartree-Fock type SCF-MO calculations. For reasons outlined above the choice of number and type of atomic orbitals (AO) is of utmost importance. In the present *ab initio* study the n individual atomic orbitals ($\underline{\chi}$) used were built up by contraction from N primitive ($\underline{\eta}$) Gaussian type function (GTF) using an $N \times n$ matrix ($\boldsymbol{T}$) in transformation (1),

$$\underline{\chi} = \underline{\eta}\,\boldsymbol{T}. \tag{1}$$

The molecular orbitals (MO) were obtained from the contracted basis ($\underline{\chi}$) by a linear transformation (2). The matrix $\boldsymbol{C}$ that performed the transformation from the contracted AO to the MO basis ($\underline{\phi}$) was obtained by the self-consistent field (SCF) method.

$$\underline{\phi} = \underline{\chi}\,\boldsymbol{C}. \tag{2}$$

Table 2. Contracted Gaussian basis sets used in calculations on C_2H_4S, C_2H_4 and S

Chemical system	Basis set size[a]		Basis set type[b]	Ref.
	Primitive	Contracted	Primitive → Contracted	
S	45	24	$(12^s, 9^p, 1^d) \rightarrow [6^s 4^p, 1^d]^c$	[28]
C	29	10	$(11^s 6^p) \rightarrow [4^s 2^p]$	[29]
H	3	1	$(3^s) \rightarrow [1^s]$	[30]
C_2H_4S	125	48	48 *spd*	—
S	39	18	$(12^s, 9^p) \rightarrow [6^s, 4^p]$	[28]
C	29	10	$(11^s, 6^p) \rightarrow [4^s, 2^p]$	[29]
H	3	1	$(3^s) \rightarrow [1^s]$	[30]
C_2H_4S	119	42	42 *sp*	—
S	39	18	$(12^s, 9^p) \rightarrow [6^s, 4^p]$	[28]
C	17	5	$(8^s, 3^p) \rightarrow [2^s 1^p]$	[30]
H	3	1	$(3^s) \rightarrow [1^s]$	[30]
C_2H_4S	85	32	32 *sp*	—

[a] The reduction in basis set size ($N \rightarrow n$) is achieved by the transformation (contraction) specified in Eq. (1) where the primitive GTF(η) are changed to contracted AO (χ).

[b] Double zeta basis sets are used in a number of cases:

$[6^s, 4^p, 1^d] \equiv [1s, 1s', 2s, 2s', 3s, 3s', 2p, 2p', 3p, 3p', 3d]$

$[4^s, 2^p] \equiv [1s, 1s', 2s, 2s', 2p, 2p']$

while single zeta (minimal Slater) basis sets turned out to be quite satisfactory in many of the cases:

$[2^s, 1^p] \equiv [1s, 2s, 2p]$

$[1^s] \equiv [1s]$.

[c] The d-orbital exponent was chosen to be 0.55.

These molecular Hartree-Fock type SCF-MO calculations have been carried out on an IBM 360/65 computer using the IBMOL-IV system [26, 27]. The three types of AO basis sets used are listed in Table 2.

Results and Discussion

Fig. 1 illustrates the total energy values of thiirane as calculated by the three basis sets (48 *spd*, 42 *sp* and 32 *sp*) used in the present study along with those of earlier studies.

The first *ab initio* MO calculation on thiirane by Clark [5], where only a minimal uncontracted Gaussian basis set was used, together with a more recent study using Slater type orbitals (STO) by Bonaccorsi *et al.* [6], are also included for comparison. As seen from the figure all three basis sets used yield near Hartree-Fock wavefunctions since the computed total energy approaches the Hartree-Fock limit. The numerical values used for the construction of Fig. 1 are summarized in Tables 1 and 3, and the molecular geometries [31] are specified in Fig. 2.

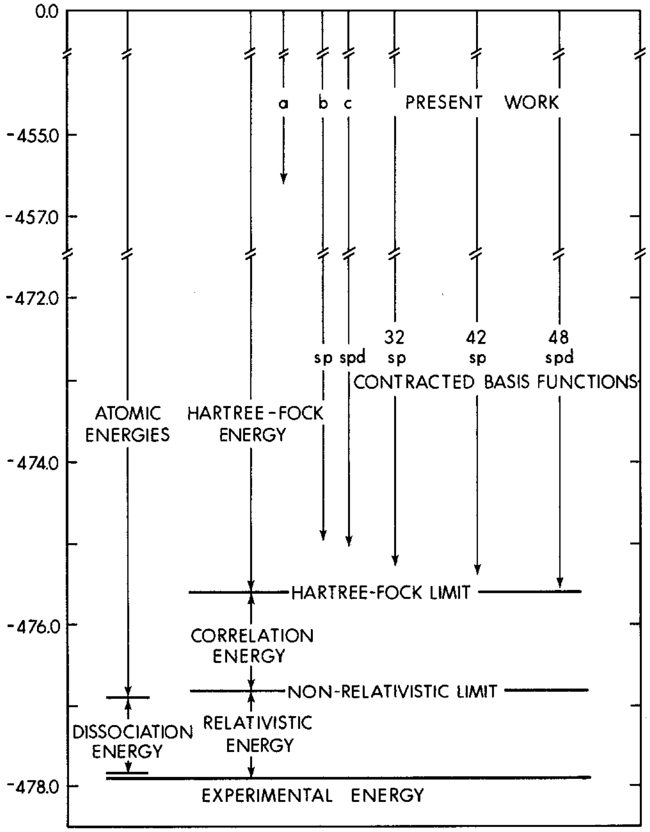


Fig. 1. The breakdown of total energy to experimental and theoretical components for thiirane. (The energy components are summarized in Table 1. Results of the *Present Work* are given in Table 3. The earlier calculations of "*a*" and "*b*" as well as "*c*" were taken from Ref. [5] and [6] respectively)

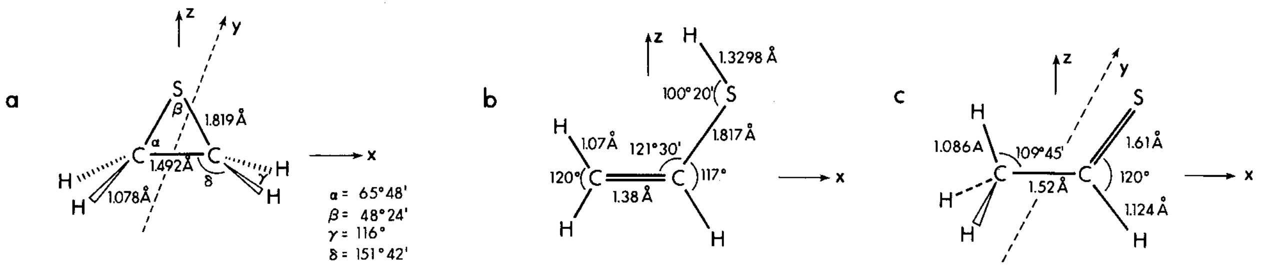


Fig. 2. Geometrical arrangements of three C_2H_4S isomers

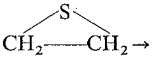
Table 3. Computed energy components and total energy values of various species

	$S(^3P)$	$S(^1D)$	S^{2-}	Ethylene		$C_2H_4^{2+}$	Thiirane[a]			Vinyl mercaptan
Contracted AO	18 *sp*	18 *sp*	18 *sp*	24 *sp*	14 *sp*	14 *sp*	48 *spd*	42 *sp*	32 *sp*	32 *sp*
Nuclear repulsion energy	0.00000	0.00000	0.00000	33.32547	33.32547	33.32547	100.99740	100.99740	100.99740	92.47674
One-electron energy	−548.52059	−548.62930	−562.07707	−168.79478	−168.96544	−156.75106	−853.38129	−853.07684	−853.40514	−835.47423
Two-electron energy	151.05866	151.21262	164.92949	57.53166	57.89642	46.80174	276.92415	276.65882	277.14553	268.12090
Total energy	−397.46193	−397.41669	−397.14758	−77.93765	−77.74355	−76.62385	−475.45974	−475.42062	−475.26221	−474.87659

[a] The dipole moments computed with the 32 *sp* and 42 *sp* basis sets are 2.69 and 1.74 Debye, respectively. The experimental value is 1.84 Debye [31].

While the total energy values of the various systems are summarized in Table 3, the corresponding energy differences are given in Table 4. The SCF orbital energies are compiled in Table 5 and shown graphically in Fig. 3. The coefficients (elements of the *C* matrix in Eq. (2)) for the four highest filled and the four lowest empty MO are given in Table 6. With the aid of these coefficients one may find a 1:1 correspondence for the orbital symmetry study used by previous authors [3, 4].

Table 4. Energy differences[a] associated with the dissociation and isomerization of thiirane

 →	$CH_2{=}CH_2 + S(^3P)$	$CH_2{=}CH_2 + S(^1D)$	$[CH_2\text{-}CH_2]^{2+} + S^{2-}$	$CH_2{=}CH{-}SH$
48 *spd*	0.06016 (37.8)	0.10540 (66.2)	—	—
42 *sp*	0.02104 (13.2)	0.06628 (41.6)	—	—
32 *sp*	0.05673 (35.6)	0.10196 (64.0)	1.49078 (935.78)	0.38621 (242.42)
Exp	(58)[b]	(84.4)[b]		

[a] Differences are given in Hartree atomic units, bracketed values represent the kcal/mole equivalent; (1.0 hartree = 627.71 kcal/mole).

[b] Ref. [23].

Table 5. Computed MO energies for thiirane

No.	Orbital	Type	48 *spd*	42 *sp*
1	$1a_1$	1σ	−91.9897	−91.9953
2	$2a_1$	2σ	−11.3526	−11.3602
3	$1b_1$	3σ	−11.3519	−11.3596
4	$3a_1$	4σ	− 8.9747	− 8.9835
5	$4a_1$	5σ	− 6.6651	− 6.6730
6	$2b_1$	6σ	− 6.6626	− 6.6701
7	$1b_2$	1π	− 6.6599	− 6.6672
8	$5a_1$	7σ	− 1.1762	− 1.1954
9	$3b_1$	8σ	− 0.8726	− 0.8802
10	$6a_1$	9σ	− 0.8559	− 0.8632
11	$2b_2$	2π	− 0.6984	− 0.7081
12	$7a_1$	10σ	− 0.6352	− 0.6395
13	$1a_2$	3π	− 0.5736	− 0.5817
14	$8a_1$	11σ	− 0.4723	− 0.4683
15	$4b_1$	12σ	− 0.4563	− 0.4577
16	$3b_2$	4π	− 0.3695	− 0.3766
17	$5b_1$	$13\sigma^*$	0.1625	0.1665
18	$9a_1$	$14\sigma^*$	0.2480	0.2380
19	$6b_1$	$15\sigma^*$	0.4504	0.4534
20	$4b_2$	$5\pi^*$	0.5503	0.5831
21	$10a_1$	$16\sigma^*$	0.5819	0.6280
22	$11a_1$	$17\sigma^*$	0.6314	0.7516
23	$7b_1$	$18\sigma^*$	0.6931	0.6883
24	$2a_2$	$6\pi^*$	0.7614	0.7961

In view of the special importance of excited states in the formation of the thiirane molecule *via* the $C_2H_4 + S$ reaction, some attention has been given to the UV spectrum of thiirane.

Table 6. Computed MO coefficients in linear combination of the 48 *spd* AO for thiirane

		Highest filled MO				Lowest vacant MO			
Atom	AO	$1a_2(3\pi)$	$8a_1(11\sigma)$	$4b_1(12\sigma)$	$3b_2(4\pi)$	$5b_1(13\sigma^*)$	$9a_1(14\sigma^*)$	$6b_1(15\sigma^*)$	$4b_2(5\pi^*)$
C_1	2*s*	0.0	0.00144	0.00722	0.0	−0.05465	0.07626	0.16489	0.0
	2*px*	0.0	−0.071314	−0.01719	0.0	−0.01450	−0.01554	−0.11842	0.0
	2*py*	0.11458	0.0	0.0	−0.03063	0.0	0.0	0.0	0.09018
	2*pz*	0.0	0.09228	−0.08786	0.0	0.11435	−0.08099	0.03068	0.0
C_2	2*s*	0.0	0.00144	−0.00722	0.0	0.05465	0.07626	−0.16489	0.0
	2*px*	0.0	0.071314	−0.01719	0.0	−0.01450	0.01554	−0.11842	0.0
	2*py*	−0.11458	0.0	0.0	−0.03063	0.0	0.0	0.0	0.09018
	2*pz*	0.0	0.09228	0.08786	0.0	−0.11435	−0.08099	−0.03068	0.0
S	3*s*	0.0	−0.18981	0.0	0.0	0.0	0.30392	0.0	0.0
	3*px*	0.0	0.0	0.21306	0.0	0.12216	0.0	0.0	0.0
	3*py*	0.0	0.0	0.0	0.26860	0.0	0.0	0.0	−0.03255
	3*pz*	0.0	−0.168170	0.0	0.0	0.0	−0.10872	0.0	0.0
	$3dx^2$	0.0	0.029257	0.0	0.0	0.0	−0.08149	0.0	0.0
	$3dy^2$	0.0	−0.01666	0.0	0.0	0.0	0.14894	0.0	0.0
	3*dxz*	0.0	0.0	−0.08757	0.0	0.15158	0.0	−0.15949	0.0
	$3dz^2$	0.0	0.06373	0.0	0.0	0.0	−0.04666	0.0	0.0
	3*dxy*	−0.01318	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	3*dyz*	0.0	0.0	0.0	−0.01643	0.0	0.0	0.0	−0.31753
H1	1*s*	0.27447	0.03248	0.11036	−0.11354	−0.03697	−0.02345	0.06871	−0.67551
H2	1*s*	−0.27447	0.03248	0.11036	0.11354	−0.03697	−0.02345	0.06871	0.67551
H3	1*s*	−0.27447	0.03248	−0.11036	−0.11354	0.03697	−0.02345	−0.06871	−0.67551
H4	1*s*	0.27447	0.03248	−0.11036	0.11354	0.03697	−0.02345	−0.06871	0.67551

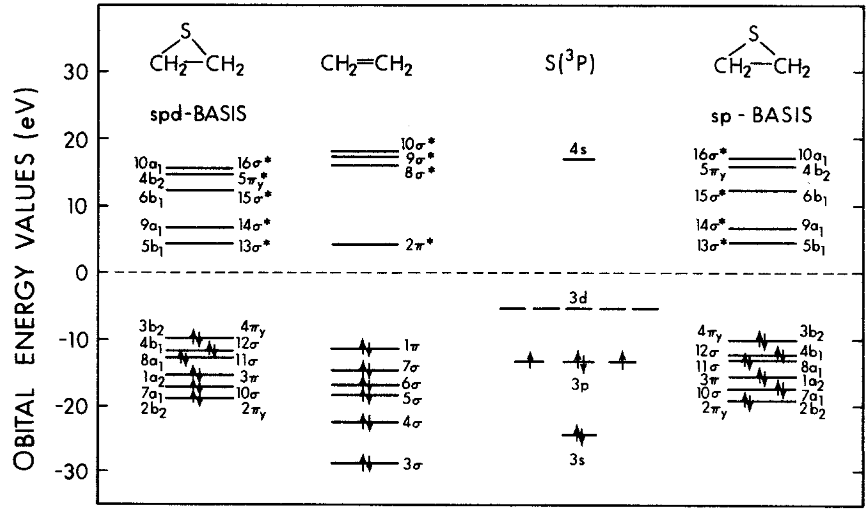


Fig. 3. A comparison of thiirane MO energies, computed from the 48 *spd* and 42 *sp*-wavefunctions, with orbital energies of sulfur and ethylene

Table 7. Transition energies[a], transition moments[b] and oscillator strengths[b] for thiirane as computed from the 48 *spd* Gaussian wavefunction

No.	Type of excitation	Transition energy[a] Singlet	Triplet	Transition moment[b] (Debye)	Oscillator strength[b]
1	$3b_2 \rightarrow 5b_1$	47002 (5.83)	41688 (5.17)	0.0248	0.000547
2	$3b_2 \rightarrow 9a_1$	68088 (8.44)	54861 (6.80)	0.0923	0.002954
3	$8a_1 \rightarrow 5b_1$	86836 (10.77)	61300 (7.60)	5.6182	0.229292
4	$4b_1 \rightarrow 9a_1$	87105 (10.80)	75547 (9.37)	1.5705	0.064295
5	$4b_1 \rightarrow 5b_1$	92597 (11.48)	55484 (6.87)	15.3109	0.666338
6	$1a_2 \rightarrow 5b_1$	99887 (12.38)	96786 (12.00)	0.0318	0.001493
7	$8a_1 \rightarrow 9a_1$	104167 (12.91)	80389 (9.96)	15.1056	0.739518
8	$7a_1 \rightarrow 5b_1$	110091 (13.65)	101757 (12.62)	1.2077	0.062453
9	$1a_2 \rightarrow 9a_1$	120610 (14.95)	118266 (14.66)	0.0035	0.000170
10	$3b_2 \rightarrow 6b_1$	122273 (15.54)	121625 (15.08)	0.0254	0.001458
11	$2b_2 \rightarrow 5b_1$	125089 (15.51)	122231 (15.15)	0.0077	0.000454
12	$4b_1 \rightarrow 6b_1$	130863 (16.22)	123456 (15.31)	0.0346	0.002126
13	$7a_1 \rightarrow 9a_1$	132117 (16.38)	121625 (15.08)	5.3596	0.332800
14	$8a_1 \rightarrow 6b_1$	137428 (17.04)	118583 (14.70)	3.8876	0.251105
15	$3b_2 \rightarrow 10a_1$	143904 (17.84)	132556 (16.43)		
16	$2b_2 \rightarrow 9a_1$	145632 (18.06)	142392 (17.65)	0.0096	0.000657
17	$1a_2 \rightarrow 6b_1$	148469 (18.41)	140879 (17.47)	0.0210	0.001467
18	$3b_2 \rightarrow 4b_2$	150403 (18.65)	141079 (17.40)	1.2778	0.090325

[a] In units of cm^{-1} (eV).

[b] For singlet → singlet transitions only.

Table 8. Transition energies[a], transition moments[b] and oscillator strengths[b] for thiirane as computed from the 42 *sp* Gaussian wavefunction

No.	Type of excitation	Transition energy[a] Singlet	Triplet	Transition moment[b] (Debye)	Oscillator strength[b]
1	$3b_2 \rightarrow 5b_1$	51763 (6.42)	48808 (5.08)	0.0	0.0
2	$3b_2 \rightarrow 9a_1$	65992 (8.18)	55743 (6.91)	0.08734	0.00257
3	$4b_1 \rightarrow 9a_1$	85487 (10.60)	61252 (7.59)	1.648405	0.06623
4	$8a_1 \rightarrow 5b_1$	88003 (10.91)	73862 (9.16)	6.916617	0.28608
5	$4b_1 \rightarrow 5b_1$	97286 (12.06)	56868 (7.05)	15.97600	0.73049
6	$1a_2 \rightarrow 5b_1$	99499 (12.34)	95883 (11.89)	0.017398	0.00081
7	$8a_1 \rightarrow 9a_1$	102961 (12.77)	76800 (9.52)	14.245229	0.68935
8	$7a_1 \rightarrow 5b_1$	108559 (13.46)	101814 (12.62)	0.723089	0.03689
9	$1a_2 \rightarrow 9a_1$	118492 (14.69)	115926 (14.37)	0.0	0.0
10	$2b_2 \rightarrow 5b_1$	125260 (15.53)	121965 (15.12)	0.0	0.0
11	$3b_2 \rightarrow 6b_1$	125295 (15.53)	124792 (15.47)	0.0	0.0
12	$7a_1 \rightarrow 9a_1$	130020 (16.12)	119552 (14.82)	3.803104	0.23241
13	$4b_1 \rightarrow 6b_1$	131919 (16.36)	125714 (15.59)	0.058187	0.00361
14	$8a_1 \rightarrow 6b_1$	135623 (16.81)	120616 (14.95)	2.149153	0.13699
15	$2b_2 \rightarrow 9a_1$	143805 (17.83)	140518 (17.42)	0.002648	0.00018
16	$1a_2 \rightarrow 6b_1$	150186 (18.62)	141916 (17.59)	0.002289	0.00016
17	$3b_2 \rightarrow 4b_2$	162054 (20.09)	157407 (19.52)	1.527925	0.11638
18	$8a_1 \rightarrow 4b_2$	167582 (20.78)	164707 (20.42)	0.008942	0.00070
19	$4b_1 \rightarrow 4b_2$	168262 (20.86)	164327 (20.37)	0.0	0.0
20	$3b_2 \rightarrow 10a_1$	173325 (21.49)	171282 (21.24)	0.288187	0.02348

[a] In units of cm^{-1} (eV).

[b] For singlet → singlet transitions only.

The first question one has to face in this regard is the type of basis set used, that is the importance of *d*-orbitals on the excitation pattern. Consequently in the study employing the largest basis set, 42 contracted *sp* basis orbitals, the effect of *d*-orbitals was examined by expanding the number of basis orbitals to 48, involving the *d*-orbitals.

The occupied and empty MO of the thiirane molecule in these two basis sets, as well as those of the reactants, are shown in Fig. 3 and the data given in Table 5. There is no marked difference in the MO patterns comparing the *sp* and *spd* basis sets. However, the energies of the various excited electronic configurations as computed by the virtual orbital technique show noticeable shifts. On closer examination one discovers that most of the differences are due to an overall lowering of the *spd* basis, manifesting the effect of the additional *d*-GTF. A fairly consistent picture may be obtained if the two ground states are chosen to be the energy zero. This is given in Tables 7, 8 and Fig. 4.

Owing to the similarity of the two patterns and the saving in computer time, it appeared permissible to choose the *sp* basis set for further studies. As an additional check the excitation energies calculated with the *spd* basis set (ΔE_{spd}) were compared with those obtained with the *sp* basis set (ΔE_{sp}) in Fig. 5. The diagonal 45° line represents the "perfect correlation" and the points seem to correlate to an acceptable degree. The first ionization potentials obtained in accordance with Koopmans' theorem from the two basis sets are also quite close to one another, however, they are numerically larger than the corresponding experimental values just as calculated excitation energies are appreciably higher than the corresponding experimental values when calculated with the virtual orbital technique.

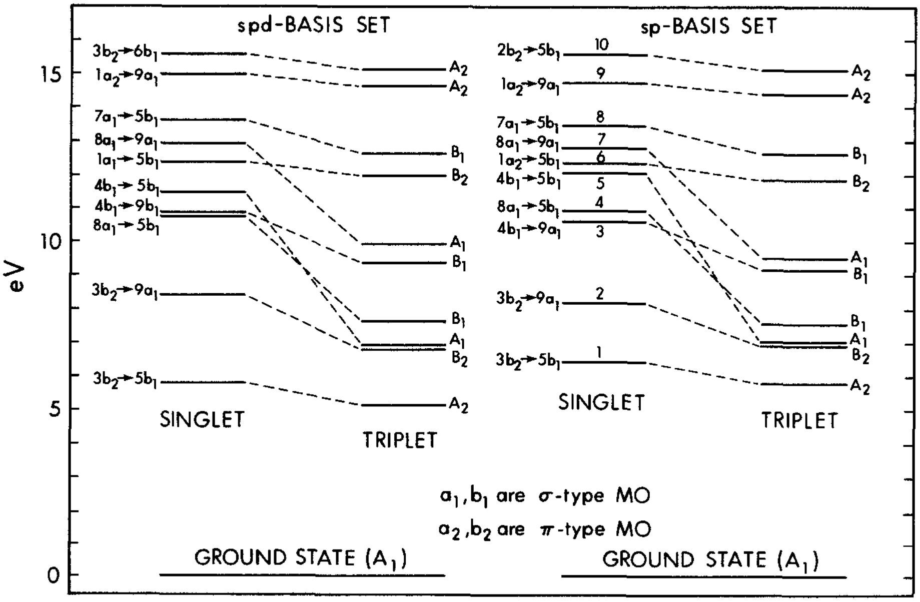


Fig 4. Excited electronic configuration energies relative to ground electronic configuration energies as computed with the 48 *spd* and 42 *sp* basis sets

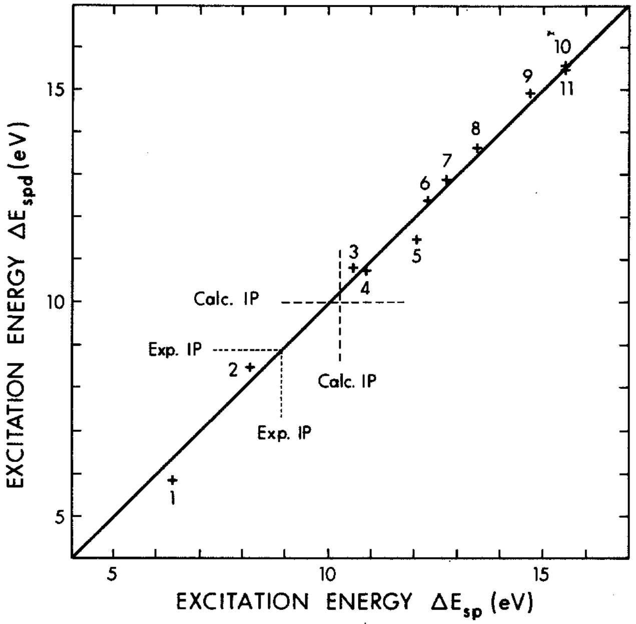


Fig. 5. Correlation of excitation energies as computed by the virtual orbital technique (*cf.* Fig. 5, and Tables 7 and 8) using the 48 *spd* and 42 *sp* basis sets

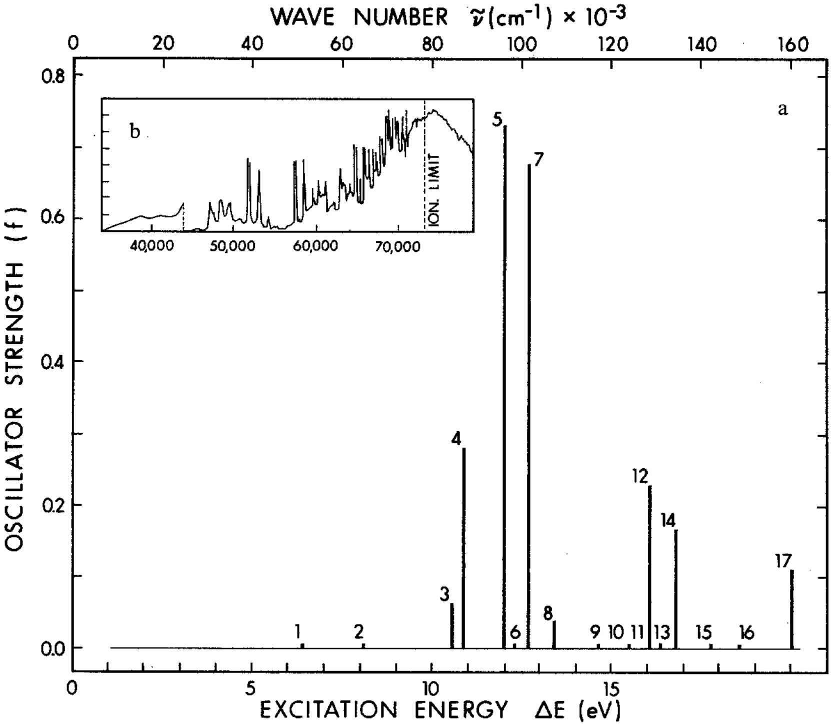
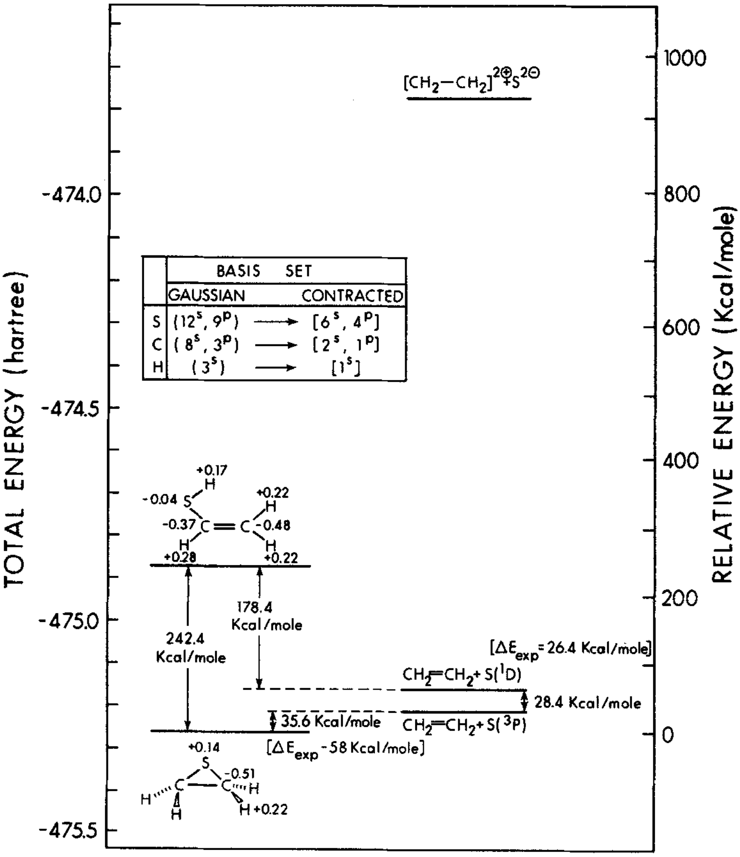


Fig. 6. a Theoretical spectrum of thiirane as computed with the 42 *sp* basis set (Table 8). b Experimental electronic spectrum of thiirane [taken from J. chem. Physics **43**, 3666 (1965)]

In the theoretical spectrum, Fig. 6a, the oscillator strength as calculated from the transition moments is given as a function of excitation energy. For comparison the experimental u.v. spectrum of thiirane is also depicted in Fig. 6b.

It is probably worth noting that while the experimentally obtained energy difference between thiirane and the $S(^3P) + C_2H_4$ system is about 58 kcal/mole, the computed energy difference is 35.6 kcal/mole. This is precisely the phenomenon that has been discussed at the beginning of this paper, that in bond formations where the number of paired electrons is increased, the Hartree-Fock wavefunction introduces a systematic error which is quite appreciable, 22 kcal/mole in the present case. On the other hand the calculated energy difference between the (^1D) and (^3P) states of the S-atom is 28.4 kcal/mole which is quite close to the experimental value of 26.4 kcal/mole. This is understandable since both states are represented by an open shell wavefunction implying the same degree of electron pairing. These energy relations are shown in Fig. 7.

Finally, one should notice that the insertion product, vinyl mercaptan, is very much higher on the energy scale than thiirane. This result was anticipated, but



	BASIS SET	
	GAUSSIAN	CONTRACTED
S	$(12^s, 9^p)$ →	$[6^s, 4^p]$
C	$(8^s, 3^p)$ →	$[2^s, 1^p]$
H	(3^s) →	$[1^s]$

Fig. 7. A comparison of total energy values computed by the *ab initio* SCF-MO method for the ground state of the various C_2H_4S isomers

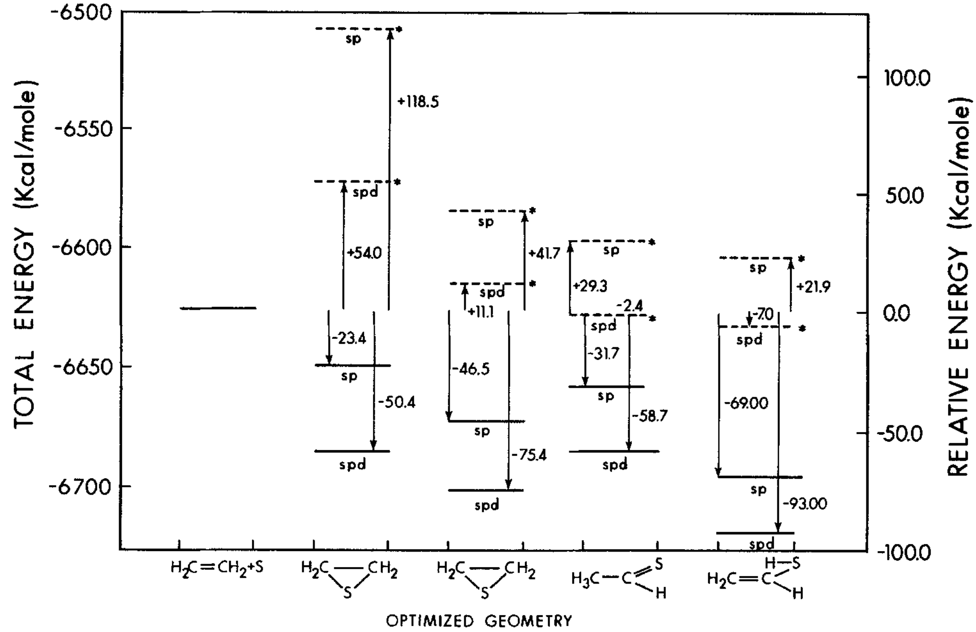


Fig. 8. A comparison of total energy values computed by the semi-empirical EHMO method for the ground and some low lying excited states of the various C_2H_4S isomers

the energy difference appears to be anomalously large and undoubtedly is partly due to the choice of geometrical parameters for vinyl mercaptan, which were based on those of the analogous vinyl halides and ethyl mercaptan molecules.

Most of the molecules studied experimentally are too large to lend themselves to the currently available technology of *ab initio* MO calculations. For this reason it seemed desirable to carry out some semi-empirical calculations at this stage so that comparison could be made between the two methods, thus providing a firm foundation for semi-empirical computations on larger molecules.

The results of Extended Hückel Molecular Orbital (EHMO) calculations, carried out analogously to our earlier work on the COS molecule [32] are presented in Fig. 8. It is interesting that the thio-enol shows an appreciable stability. This seems to indicate that the conjugative stabilization is overemphasized by the EHMO method with respect to that of the *ab initio* SCF-MO theory.

Returning to the problem of the addition reaction profile it is seen from the correlation diagram in Fig. 9 that the addition of $S(^1D)$ atom to ethylene is energetically an inviting process to form ground state $(^1A_1)$ thiirane. The $S(^3P)$ atom addition to give the lowest vertical triplet excited state of thiirane, however, appears to be endothermic by both the *ab initio* and EHMO calculations and would require an appreciable activation energy, contrary to experiment. Therefore, this process is not as simple as implied by earlier qualitative reasoning [3, 4]. A plausible alternative to resolve the discrepancy is the assumption that the ring distorted geometry of the lowest excited triplet state of thiirane, corresponding

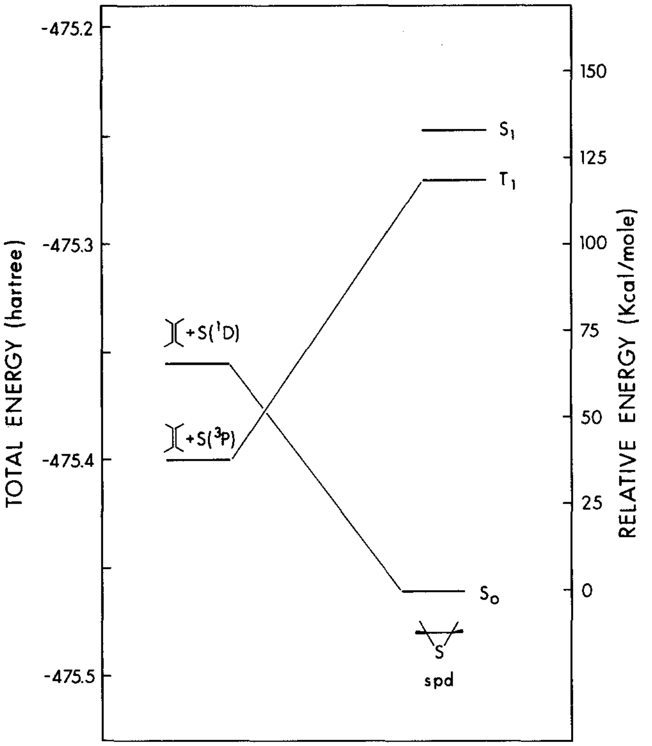


Fig. 9. Comparison of some low lying electronic configuration energies for the initial and final states of $CH_2=CH_2 + S \rightarrow C_2H_4S$ as computed with the 48 *spd* basis set

to a non-vertical excitation, is considerably more stable than the symmetric species as proposed earlier [33] purely on experimental grounds. This aspect of the problem is the subject of current investigations which will be reported at a later date [7].

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