

# Ground States of Molecules. 56.\* MNDO Calculations for Molecules Containing Sulfur

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MNDO has been extended to sulfur, but without inclusion of  $3d$  AOs. Calculations are reported for heats of formation, geometries, dipole moments, and ionization energies of a variety of sulfur-containing molecules. The average discrepancy between calculated and observed heats of formation is larger than for compounds of other elements, a difference probably due, at least partly, to the lower accuracy of the thermochemical data for sulfur compounds. The calculated dipole moments agree well with experiment as do the calculated ionization energies, except for those corresponding to ionization from sulfur "lone-pair" orbitals which are too high by ca. 1 eV, probably as a result of the neglect in MNDO of interactions between inner and valence shell orbitals. As in the case of other third-period elements, the calculated heats of formation of compounds of sulfur in its higher valence states ( $S^{IV}$ ,  $S^{VI}$ ) were too positive by large amounts, due presumably to the neglect of  $3d$  AOs.

## INTRODUCTION

Previous articles of this series have described the theoretical background<sup>1</sup> of the MNDO method

\* See Part 55 in this series: M. J. S. D. Dewar and S. Olivella, *J. Am. Chem. Soc.*, **101**, 4958 (1979).

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and parameters for carbon, hydrogen, nitrogen and oxygen,<sup>2</sup> boron,<sup>3</sup> fluorine,<sup>4</sup> beryllium,<sup>5</sup> and chlorine.<sup>6</sup> Here we describe its extension to sulfur, at present without inclusion of  $3d$  AOs, and calculations for a wide variety of sulfur-containing molecules. The parameters for sulfur were reported in a preliminary communication.<sup>7</sup>

**Table I.** MNDO parameters for sulfur.<sup>a</sup>

Optimized Parameters	Value	Derived Parameters	Value
$U_{ss}, \text{eV}$	-75.239152	$H_F^A, \text{kcal/mol}$	66.40
$U_{pp}, \text{eV}$	-57.832013	$E_{el}^A, \text{eV}$	-235.45636
$\zeta_s, \text{au}$	2.613591	$D_1^{\circ}, \text{\AA}$	0.435589
$\zeta_p, \text{au}$	2.034393	$D_2^{\circ}, \text{\AA}$	0.435248
$B_s, B_p, \text{eV}$	-11.142231	$\rho_C^{\circ}, \text{\AA}$	0.558953
$\alpha, \text{\AA}^{-1}$	2.4916445	$\rho_1^{\circ}, \text{\AA}$	0.449254
		$\rho_2^{\circ}, \text{\AA}$	0.468321

<sup>a</sup> See ref. 7.

Table II. Heats of formation.





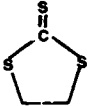
Molecule <sup>a</sup>	Heat of Formation (kcal/mole)				
	Cal.	Obs.	Error	Corrected <sup>b</sup>	Error
$S_2(^3\Sigma)$	24.9	30.8 <sup>c</sup>	- 5.9	29.9	- 0.9
$SO(^3\Sigma)$	10.3	1.6 <sup>c</sup>	8.7	10.3	8.7
*SSi	0.9	16.9 <sup>c</sup>	-16.0	0.9	-16.0
*COS	-29.4	-33.8 <sup>d</sup>	4.4	-32.4	1.4
*CS <sub>2</sub>	30.3	28.0 <sup>d</sup>	2.3	24.3	- 3.7
*H <sub>2</sub> S	1.7	- 4.9 <sup>c</sup>	6.6	- 4.3	0.6
H <sub>2</sub> S <sub>2</sub>	0.7	3.9 <sup>e</sup>	- 3.2	- 0.3	- 4.2
H <sub>2</sub> S <sub>3</sub>	- 1.7	3.6 <sup>f</sup>	- 5.3	2.3	- 1.3
H <sub>2</sub> S <sub>4</sub>	- 3.6	5.7 <sup>f</sup>	- 9.2	5.4	- 0.3
H <sub>2</sub> S <sub>5</sub>	- 5.7	8.0 <sup>f</sup>	-13.7	8.3	0.3
*SF <sub>2</sub>	-35.9	-51.8 <sup>e</sup>	15.9	g	
S <sub>2</sub> F <sub>2</sub>	-29.9	-54.5 <sup>e</sup>	24.6	g	
*SCl <sub>2</sub>	-20.0	- 5.2 <sup>e</sup>	-15.9	-10.0	- 4.8
*S <sub>2</sub> Cl <sub>2</sub>	-22.1	- 4.8 <sup>e</sup>	-16.3	- 7.1	- 2.3
*S(CH <sub>3</sub> ) <sub>2</sub>	-17.4	- 8.9 <sup>d</sup>	- 8.5	- 7.4	1.5
*S <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>	-18.9	- 5.6 <sup>d</sup>	-13.3	- 3.9	1.7
*S <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	-21.8	0.0 <sup>h</sup>	-21.8	- 1.8	- 1.8
S <sub>2</sub> (CN) <sub>2</sub>	75.9	82.3 <sup>d</sup>	- 6.4	90.9	8.6
*CH <sub>3</sub> SH	- 8.5	- 5.4 <sup>d</sup>	- 3.0	- 6.5	- 1.1
CH <sub>3</sub> CH <sub>2</sub> SH	-14.6	-11.0 <sup>d</sup>	- 3.6	-12.6	- 1.6
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SH	-19.4	-16.2 <sup>i</sup>	- 3.2	-17.4	- 1.2
(CH <sub>3</sub> ) <sub>2</sub> CH SH	-17.5	-18.1 <sup>j</sup>	0.6	-15.5	2.6
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> SH	-24.1	-21.1 <sup>i</sup>	- 3.0	-22.1	- 1.0
PhSH	24.5	26.9 <sup>d</sup>	- 2.4	26.5	- 0.4
HSCH <sub>2</sub> CH <sub>2</sub> SH	- 8.8	- 2.2 <sup>d</sup>	- 6.6	- 4.8	- 2.6
HNCS	38.0	30.0 <sup>k</sup>	8.0	35.0	5.0
*CH <sub>3</sub> NCS	30.5	27.1 <sup>e</sup>	3.4	27.5	0.4
	13.8	19.7 <sup>d</sup>	-5.9	23.8	4.1
	- 7.1	14.6 <sup>d</sup>	-21.7	2.9	-11.7
	-24.9	-8.1 <sup>d</sup>	-16.8	-14.9	- 6.8

Table II (continued from previous page)

Molecule <sup>a</sup>	Heat of Formation (kcal/mole)				
	Cal.	Obs.	Error	Corrected <sup>b</sup>	Error
	30.0	27.6 <sup>d</sup>	2.4	g	
	9.2	22.7 <sup>d</sup>	-13.5	26.2	3.5
S <sub>4</sub>	27.6	32.7 <sup>f</sup>	- 5.1	47.6	14.9
S <sub>6</sub>	- 0.4	24.5 <sup>f</sup>	-24.9	29.6	5.1
S <sub>8</sub>	-13.7	24.5 <sup>f</sup>	-38.2	26.3	1.8
SO <sub>2</sub>	27.5	-70.9 <sup>c</sup>	98.4	g	
SO <sub>3</sub>	109.7	- 94.6 <sup>f</sup>	204.3	g	
OSF <sub>2</sub>	-13.2	-130.0 <sup>c</sup>	116.8	g	
OSCl <sub>2</sub>	- 3.1	- 50.8	47.7	g	
H <sub>2</sub> SO <sub>4</sub>	45.2	-177.0 <sup>c</sup>	222.2	g	

<sup>a</sup> Molecules with asterisks used in basis set for parametrization. <sup>b</sup> Calculated values corrected for systematic errors, as indicated in text. <sup>c</sup> D. R. Stull and H. Prophet, *JANAF Thermochemical Tables, NSRDS-NBS 37*, 2nd ed., 1971. <sup>d</sup> J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic, New York, 1970. <sup>e</sup> S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). <sup>f</sup> D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, *Selected Values of Chemical Thermodynamic Properties, Part 1*, NBS, Washington, D.C., 1965, pp. 270-271. <sup>g</sup> See text. <sup>h</sup> B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **67**, 1283 (1963). <sup>i</sup> R. E. Pennington, D. W. Scott, H. L. Finke, J. P. McCullough, J. F. Messerly, I. A. Hossenlopp, and G. Waddington, *J. Am. Chem. Soc.*, **78**, 3266 (1956). <sup>j</sup> J. P. McCullough, H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, R. E. Pennington, and G. J. Waddington, *Am. Chem. Soc.*, **76**, 4796 (1954). <sup>k</sup> M. F. Guest, J. B. Pedley, and M. Horn, *J. Chem. Thermodyn.*, **1**, 345 (1969).

## PROCEDURE

For third-period elements, a minimum basis set of valence shell (3s, 3p) AOs is used, the valence electrons being assumed to move in the field due to a core composed of the nuclei and inner shell (1s, 2s, 2p) electrons. The optimized parameters for sulfur (Table I) were obtained by the same procedure as before,<sup>7</sup> by a least-squares fit to the observed properties of a basis set of 13 molecules (indicated by asterisks in Table II). The properties (number of molecules) used were heats of formation (13), ionization energies (7), and dipole moments (7), together with 12 bond lengths, eight bond angles, and three dihedral angles. The calculations of geometries and molecular properties followed exactly the same course as that used previously,<sup>1-6</sup> using the previously reported<sup>1-6</sup> parameters for elements other than sulfur.

## RESULTS AND DISCUSSION

### Heats of Formation and Dipole Moments

Table II displays the heats of formation and dipole moments calculated for 83 sulfur-containing compounds, together with experimental values where these are available.

It will be seen that the calculated heats of formation for compounds of sulfur in its higher valence states are too positive by very large amounts. Similar discrepancies have been noted in analogous MNDO calculations for other third-period elements in their higher valence states<sup>6</sup> and are clearly due to the neglect of 3d AOs in MNDO. *Ab initio* calculations<sup>8-10</sup> indicate that 3d AOs make significant contributions to bonding in such cases and also lead to a decrease in molecular polarity.

Table III. Dipole moments and ionization energies.


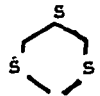


Compound	Dipole Moment (D)		Vertical Ionization Energy	
	Calc.	Obs.	Calc.	Obs.
COS	0.93	0.71 <sup>a</sup>	11.07	-
CS <sub>2</sub>	0	0	10.59	10.08 <sup>b</sup>
H <sub>2</sub> S	1.59	0.97 <sup>c</sup>	10.65	10.43 <sup>d</sup>
H <sub>2</sub> S <sub>2</sub>	1.58	-	10.75	10.01 <sup>e</sup>
SF <sub>2</sub>	2.02	1.05 <sup>c</sup>	11.27	-
SF <sub>2</sub> F <sub>2</sub>	1.77	1.45 <sup>c</sup>	11.71	10.84 <sup>e</sup>
SCl <sub>2</sub>	0.76	0.36 <sup>f</sup>	11.04	9.70 <sup>g</sup>
S(CH <sub>3</sub> ) <sub>2</sub>	1.73	1.55 <sup>a</sup>	10.07	8.65 <sup>h</sup>
S(CN) <sub>2</sub>	1.92	3.01	11.41	11.32 <sup>i</sup>
CH <sub>3</sub> SH	1.68	1.52 <sup>c</sup>	10.33	9.44 <sup>h</sup>
CH <sub>3</sub> CH <sub>2</sub> SH	1.63	1.52 <sup>c</sup>	10.29	9.21 <sup>j</sup>
H <sub>2</sub> CS	2.53	1.65 <sup>c</sup>	9.98	9.34 <sup>k</sup>
CH <sub>3</sub> CHS	2.75	-	9.87	8.98 <sup>l</sup>
(CH <sub>3</sub> ) <sub>2</sub> CS	2.87	-	9.78	8.60 <sup>l</sup>
H <sub>2</sub> C=C=S	1.93	-	9.23	8.89 <sup>m</sup>
	2.24	-	10.17	9.05 <sup>n</sup>
	2.29	-	10.53	8.83 <sup>l</sup>
	0.90	0.53 <sup>c</sup>	9.51	8.9 <sup>o</sup>
S <sub>8</sub>	0	0	11.02	9.23 <sup>p</sup>
	4.00	-	9.11	8.11 <sup>q</sup>
SO <sub>2</sub>	3.46	1.61 <sup>a</sup>	11.79	12.31 <sup>r</sup>

Table III. Dipole moments and ionization energies.

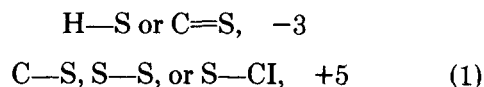
Compound	Dipole Moment (D)		Vertical Ionisation Energy	
	Calc.	Obs.	Calc.	Obs.
$(\text{CH})_3\text{S}=\text{O}$	5.97	3.96 <sup>c</sup>	8.57	
$\text{F}_2\text{SS}_2$	3.25	1.03 <sup>s</sup>	11.01	10.68 <sup>t</sup>

<sup>a</sup> A. L. McClellan, *Table of Experimental Dipole Moments*, Freeman, San Francisco, 1963, Vol. 1. <sup>b</sup> M.-J. Huben-Franskin, J. Delwiche, P. Natalis, and G. Caprace, *J. Electron. Spectrosc. Relat. Phenom.*, **18**, 295 (1980). <sup>c</sup> Volume 2 of ref. a. <sup>d</sup> G. Wagner and H. Bock, *Chem. Ber.*, **107**, 68 (1974). <sup>e</sup> B. Solouki, and H. Bock, *Inorg. Chem.*, **16**, 665 (1977). <sup>f</sup> J. T. Murray, O. Williams, and T. L. Weatherly, *Bull. Am. Phys. Soc.*, **17**, 575 HM11 (1973). <sup>g</sup> B. Solouki, P. Rosmus, and H. Bock, *Chem. Phys. Lett.*, **26**, 20 (1974). <sup>h</sup> D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell, and R. A. McLean, *J. Phys. Chem.*, **76**, 1030 (1972). <sup>i</sup> P. Rosmus, H. Stafast, and H. Bock, *Chem. Phys. Lett.*, **34**, 275 (1975). <sup>j</sup> Appearance potential: I. Omura, K. Higasi, and H. Baba, *Bull. Chem. Soc. Jpn.*, **29**, 504 (1956). <sup>k</sup> B. Solouki, P. Rosmus, and H. Bock, *J. Am. Chem. Soc.*, **98**, 6054 (1976). <sup>l</sup> H. W. Korto, B. M. Landsberg, R. J. Suffolk, and A. Vodden, *Chem. Phys. Lett.*, **29**, 265 (1974). <sup>m</sup> H. Bock, B. Solouki, G. Bert, and P. Rosmus, *J. Am. Chem. Soc.*, **99**, 1663 (1977). <sup>n</sup> D. H. Aue, H. M. Webb, W. R. Davidson, M. Vidal, M. T. Bowers, H. Goldwhite, L. E. Vertal, J. E. Douglas, P. A. Kollman, and G. L. Kenyon, *J. Am. Chem. Soc.*, **102**, 5151 (1980). <sup>o</sup> P. J. Derrick, L. Asbrink, O. Edqvist, B. O. Jonsson, and E. Lindholm, *Int. J. Mass. Spectrosc. Ion Phys.*, **6**, 177 (1971). <sup>p</sup> R. Boschi and W. Schmidt, *Inorg. Nucl. Chem. Lett.*, **9**, 643 (1973). <sup>q</sup> R. Gleiter, V. Hornung, B. Linderg, S. Hoeberg, and N. Loza'o'h, *Chem. Phys. Lett.*, **11**, 401 (1971). <sup>r</sup> H. Bock, B. Solouki, P. Rosmus, and R. Stendel, *Angew. Chem. Int. Ed. Engl.*, **12**, 933 (1973). <sup>s</sup> R. L. Kuczkowski, *J. Am. Chem. Soc.*, **86**, 3617 (1964). <sup>t</sup> G. Wagner, H. Bock, R. Budenz, and F. Seel, *Chem. Ber.*, **106**, 1285 (1973).

It will be seen (Table II) that the calculated dipole moments for compounds of  $\text{S}^{\text{IV}}$  and  $\text{S}^{\text{VI}}$  are greatly overestimated.

The agreement between the calculated and observed heats of formation and dipole moments for compounds of divalent sulfur (Table II) is comparable with that found previously for compounds containing only second-period elements,<sup>2</sup> particularly in view of the uncertain accuracy of the thermochemical data for some compound where the discrepancies are large (e.g.,  $\text{B}_2\text{S}_3$ ,  $\text{S}_2\text{F}_2$ ). While the average error is greater than that for compounds containing only second-period elements, the accuracy should be sufficient for many purposes, particularly since the errors are small for typical organic sulfides and thiols, including aromatic types. Thus the mean absolute error in the heats of formation calculated for the organic monosulfides listed in Table II is 6.5 kcal/mol.

The results in Table II, moreover, indicate the presence of systematic errors, due to over- or underestimation of the strengths of specific bonds. Thus, application of the following corrections (kcal/mol per bond) containing sulfur gives much better agreement with experiment, as the last two columns of Table II show:



The only remaining errors greater than 10 kcal/mol are for thietane,  $\text{S}_4$ ,  $\text{SiS}$ ,  $\text{SF}_2$ , and  $\text{S}_2\text{F}_2$ . MNDO is known<sup>2</sup> to give generally poor results for diatomic molecules in general and this is true in particular for CO, the second-period analog of  $\text{SiS}$ . The errors for  $\text{SF}_2$  and  $\text{S}_2\text{F}_2$  may well be due to neglect of 3d AOs of sulfur because the large charges induced by polarity of the SF bond (S positive, F negative) should increase the importance of dative  $p:d$  bonding from fluorine to sulfur. If these three compounds are omitted, the average absolute error in the "corrected" heats of formation is only 3.4 kcal/mol, while if  $\text{S}_4$  and thietane are also omitted on the grounds that MNDO overestimates the stabilities of four-membered rings and that the experimental heat of formation of  $\text{S}_4$  is somewhat uncertain, the average absolute error falls to 3.0 kcal/mol.

The calculated dipole moments (Table III) follow a similar pattern, the values for compounds of divalent sulfur being in quite good agreement with experiment while those for compounds of sulfur in its higher valence states are much too large. Ab

**Table IV.** Geometrical parameters.

MOLECULE	GROUP	BOND LENGTHS (AB $\overset{\circ}{\text{\AA}}$ ), BOND ANGLES (ABC $\overset{\circ}{\text{\AA}}$ ), and DIHEDRAL ANGLES (ABCD $\overset{\circ}{\text{\AA}}$ )	REF.
SS ( $^3\Sigma$ )	$D_{\infty h}$	1.753 (1.889)	a
OS ( $^3\Sigma$ )	$C_{\infty v}$	1.448 (1.493)	a
SiS	$C_{\infty v}$	1.804 (1.929)	b
CS	$C_{\infty v}$	1.489 (1.534)	a
SH $\cdot$	$C_{\infty v}$	1.296 (1.340)	b
SB $\cdot$	$C_{\infty v}$	1.498 (1.609)	b
SN $\cdot$	$C_{\infty v}$	1.435 (1.495)	b
SP $\cdot$	$C_{\infty v}$	1.731 (1.92)	b
OCS	$C_{\infty v}$	CS 1.512(1.559) OC 1.176 (1.159)	c
CS <sub>2</sub>	$D_{\infty h}$	CS 1.491 (1.553)	b
HBS	$C_{\infty v}$	BS 1.485 (1.599) BH 1.139 (1.169)	d
H <sub>2</sub> S	$C_{2v}$	HS 1.302(1.328) HSH 96.4(92.2)	e
H <sub>2</sub> S <sub>2</sub>	$C_2$	HS 1.308(1.327) SS1.912(2.055) HSS 103.6(91.3) HSSH99.5(90.5)	f
H <sub>2</sub> S <sub>3</sub>	$C_2$	HS 1.308 SS 1.914 HSS 101.4 SSS 107.6 HSSS 89.8	
HS <sup>1</sup> S <sup>2</sup> S <sup>3</sup> S <sup>4</sup> H	$C_2$	HS 1.309 S <sup>1</sup> S <sup>2</sup> 1.911 S <sup>2</sup> S <sup>3</sup> 1.921 SSS 108.4 HSSS 88.0 SSSS 82.8	
HS <sup>1</sup> S <sup>2</sup> S <sup>3</sup> S <sup>4</sup> S <sup>5</sup> H	$C_2$	HS 1.918 S <sup>1</sup> S <sup>2</sup> 1.911 S <sup>2</sup> S <sup>3</sup> 1.918 SSH 1.309 S <sup>1</sup> S <sup>2</sup> S <sup>3</sup> 108.3 S <sup>2</sup> S <sup>3</sup> S <sup>4</sup> 109.3 HSSS 88.0 SSSS 82.0	
SF <sub>2</sub>	$C_{2v}$	FS 1.569 (1.589) FFSF 99.9(98.3)	g

Table IV (continued from previous page)


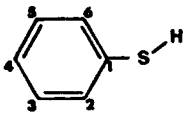
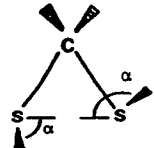
MOLECULE	GROUP	BOND LENGTHS (AB, Å), BOND ANGLES (ABC°), and DIHEDRAL ANGLES (ABCD°)	REF.
$F_2S_2$	$C_2$	FS 1.571(1.635) SS 1.944(1.888) h FS 106.0(108.3) FSSF 87.9(87.9)	
$SCl_2$	$C_{2v}$	ClS 1.960(2.014) ClSU 106.4(102.8) i	
$Cl_2S_2$	$C_2$	ClS 1.966(1.97) SS 1.901(2.07) j ClSS 107.8(107.0) ClSSCl 90.8(82.5)	
$(CH_3)_2S$	$C_{2v}$	CS 1.733(1.820) CSC 107.5(105.0) k	
$(CH_3)_2S_2$	$C_2$	CS 1.735 (1.810) SS 1.924(2.038) l CSS 106.4 (102.8) CSSC 105.2(84.7)	
$(CH_3)_2S_3$	$C_2$	CS 1.736 SS 1.919 CSS 107.3 SSS 107.7 HSSS 91.4	
$CH_3S^1S^2S^3S^4CH_3$	$C_2$	$S^1C$ 1.736 $S^1S^2$ 1.917 $S^2S^3$ 1.919 $CS^1S^2$ 107.5 $S^1S^2S^3$ 108.6 $S^1S^2S^3S^4$ 81.2 $CS^1S^2S^3$ 89.4	
$N \equiv C - \overset{\text{S}}{\text{C}} \equiv N$	$C_{2v}$	CS 1.632(1.701) CN 1.161(1.157) m CSC 101.9(98.4) NCS 177.0(170.0)	
$(NC)_2S_2$	$C_2$	CS 1.624 CN 1.163 SS 1.944 CSC 104.7 NCS 177.3 CSSC 93.4	
$CH_3SH$	$C_s$	CS 1.727 (1.818) HS 1.305(1.329) n CSH 100.8(100.3) HSCH 180.0(180.0)	
	$C_s$	HS 1.305(1.352) CS 1.738(1.810) HSC 100.3(105.1) CC 1.525 CCS 111.0	
	$C_s$	HS 1.305 CS 1.691 $C^1C^2$ 1.412 $C^2C^3$ 1.406 $C^3C^4$ 1.404 $C^4C^5$ 1.406 $C^5C^6$ 1.406 $C^6C^1$ 1.412 HSC 101.8	
	$C_2$	HS 1.306 CS 1.728 HSC 101.6 SCS 115.1 $\alpha$ 65.8	

Table IV (continued from previous page)

MOLECULE	GROUP	BOND LENGTHS (AB, Å), BOND ANGLES (ABC°), and DIHEDRAL ANGLES (ABCD°)	REF.
	C <sub>2h</sub>	HS 1.305 CS 1.740 CC 1.529 HCS 100.1 CCS 109.7	
	C <sub>s</sub>	CS 1.510 CN 1.217 NH .990 NCS 170.2 CNH 133.2	
	C <sub>s</sub>	CS 1.517 (1.597) CN 1.202 (1.192) p NC 1.432(1.479) NCS 172.4 CNC 152.0 (141.6)	
	C <sub>2v</sub>	CS 1.752 CC 1.501	
	C <sub>3v</sub>	CS 1.735 (1.810) SCS 115.6(106.5) r CSC 106.7 (106.5)	
	C <sub>2v</sub>	CS 1.692 (1.714) C=C 1.368 (1.370) s CC 1.456 (1.423)	
	C <sub>2v</sub>	C <sup>2</sup> S <sup>1</sup> 1.638 (1.667) S <sup>1</sup> S <sup>5</sup> 2.063(2.351) t C <sup>4</sup> S <sup>5</sup> 1.687(1.719) C <sup>2</sup> C <sup>3</sup> 1.388(1.368) C <sup>3</sup> C <sup>4</sup> 1.423(1.418) C <sup>3</sup> C <sup>2</sup> S <sup>1</sup> 117.0(120.1) C <sup>2</sup> C <sup>3</sup> C <sup>4</sup> 117.0(118.6) C <sup>3</sup> C <sup>4</sup> S <sup>5</sup> 116.6(119.7) C <sup>4</sup> S <sup>5</sup> S <sup>1</sup> 95.0 (89.2)	
SCF <sub>2</sub>	C <sub>2v</sub>	CS 1.573(1.589) CF 1.317(1.315) u FCS 125.8 (126.5)	
SCCl <sub>2</sub>	C <sub>2v</sub>	CS 1.533 CCl 1.744 ClCS 124.2	
	D <sub>2d</sub>	SS 1.962 α 155.4	



Table IV (continued from previous page)

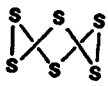

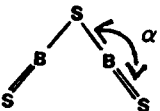
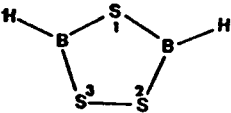

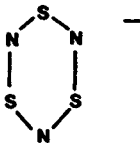
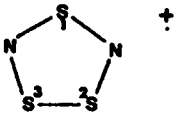
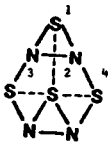
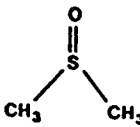
MOLECULE	GROUP	BOND LENGTHS ( $\text{\AA}$ ), BOND ANGLES ( $^\circ$ ), and DIHEDRAL ANGLES ( $^\circ$ )	REF.
	$D_{3d}$	SS 1.931 (2.057) SSS 104.2(102.2) v SSSS 71.0 (74.5)	
	$D_{4d}$	SS 1.918 (2.048) SSS 107.5(107.9) w SSSS 99.4 (98.6)	
	$C_{2v}$	BS 1.687 (1.81) B=S 1.485(1.65) x BSB 97.8 (96.0) $\alpha$ 176.2	
	$C_{2v}$	BS <sup>1</sup> 1.719 BS <sup>2</sup> 1.705 y SS 1.951(2.076) BS <sup>1</sup> B 98.9(101.6) S <sup>1</sup> BS <sup>2</sup> 119.4(117.7) BS <sup>2</sup> S <sup>3</sup> 101.2(101.5)	
	$D_{2h}$	NS 1.621 (1.654) SNS 95.0 (90.4) z NSN 85.0 (89.6)	
	$C_{3h}$	NS 1.600 (1.61) SNS 120.5 aa NSN 119.5	
	$C_{2v}$	NS <sup>1</sup> 1.568 (1.560) NS <sup>2</sup> 1.563(1.606) bb S <sup>2</sup> S <sup>3</sup> 2.016 (2.147) NS <sup>1</sup> N 101.0(107.2) S <sup>1</sup> NS <sup>2</sup> 122.1 (119.9) NS <sup>3</sup> S <sup>2</sup> 97.4(96.6)	
	$C_{2v}$	S <sup>1</sup> S <sup>2</sup> 3.664(2.586) S <sup>3</sup> S <sup>4</sup> 4.212 (2.576) cc NS <sup>1</sup> 1.712 (1.596) S <sup>1</sup> S <sup>3</sup> 2.958 (2.679) NS <sup>3</sup> 1.667 (1.617) NN 1.355 (2.560)	
SO <sub>2</sub>	$C_{2v}$	OS 1.472(1.431) OSO 106.6(119.3) c	
SO <sub>3</sub>	$D_{3h}$	OS 1.493 (1.43) b	

Table IV (continued from previous page)

MOLECULE	GROUP	BOND LENGTHS (Å), BOND ANGLES (°), and DIHEDRAL ANGLES (°)	REF.
O=SF <sub>2</sub>	C <sub>2v</sub>	OS 1.473 (1.420) FS1.610 (1.583) OSF 103.2 (106.2)	dd
O=SCl <sub>2</sub>	C <sub>2v</sub>	OS 1.463 (1.443) ClS 2.027(2.076) OSCl 107.3 (106.3)	ee
	C <sub>s</sub>	OS 1.522 CS 1.791 CSO 123.8 CSOC 141.8	

<sup>a</sup> G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*, Van Nostrand, New York, 1950. <sup>b</sup> D. R. Stull and H. Prophet, *JANAF Thermochemical Tables, NSRDS-NBS 37, 2nd ed.*, 1971. <sup>c</sup> J. K. G. Watson, *J. Mol. Spectrosc.*, **48**, 479 (1973). <sup>d</sup> E. F. Pearson and R. V. McCormick, *J. Chem. Phys.*, **58**, 1619 (1973). <sup>e</sup> H. C. Allen, Jr. and E. K. Plyler, *J. Chem. Phys.*, **25**, 1132 (1956). <sup>f</sup> G. Winnewisser, M. Winnewisser, and W. Gordy, *J. Chem. Phys.*, **49**, 3465 (1968). <sup>g</sup> D. R. Johnson and F. X. Powell, *Science*, **164**, 950 (1969). <sup>h</sup> G. Wagner, H. Bock, R. Budenz, and F. Seel, *Chem. Ber.*, **106**, 1285 (1973). <sup>i</sup> J. T. Murray, O. Williams, and T. L. Weatherly, *Bull. Am. Phys. Soc.*, **17**, 575 HM11 (1973). <sup>j</sup> E. Hirota, *Bull. Chem. Soc. Jpn.*, **31**, 130 (1958). <sup>k</sup> L. O. Brockway and H. O. Jenkins, *J. Am. Chem. Soc.*, **58**, 2036 (1936). <sup>l</sup> R. Sutter, H. Driezler, and F. Z. Rudolph, *Naturforschung A*, **20**, 1676 (1965). <sup>m</sup> P. Rosmus, H. Stafast, and H. Bock, *Chem. Phys. Lett.*, **34**, 275 (1975). <sup>n</sup> R. W. Kilb, *J. Chem. Phys.*, **23**, 1736 (1955). <sup>o</sup> L. E. Sutton, *Chem. Soc. Spec. Publ. No. 11* (1958); No. 18 (1965). <sup>p</sup> D. W. W. Anderson, D. W. H. Rankin, and A. Robertson, *J. Mol. Struct.*, **14**, 385 (1972). <sup>q</sup> K. Karakida and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **48**, 1691 (1975). <sup>r</sup> O. Hassell and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947). <sup>s</sup> B. Bak, D. Christensen, L. Hansen-Hygaard, and J. Rastrup-Anderson, *J. Mol. Spectrosc.*, **7**, 58 (1961). <sup>t</sup> L. K. Hansen and A. Hordvik, *Acta Chem. Scand.*, **24**, 2246 (1970). <sup>u</sup> A. J. Careless, H. W. Kroto, and B. M. Landsberg, *Chem. Phys.*, **1**, 371 (1973). <sup>v</sup> J. Donohue, A. Caron, and E. J. Goldish, *Am. Chem. Soc.*, **83**, 3748 (1961). <sup>w</sup> A. Caron and J. Donohue, *Acta Crystallogr.*, **18**, 562 (1965). <sup>x</sup> P. A. Akishin and V. P. Spiridonov, *Dokl. Akad. Nauk SSSR*, **129**, 1109 (1959); *Chem. Abstr.* **55**, 26607f (1959). <sup>y</sup> Methyl-substituted structure: H. M. Seip, R. Seip, and W. Seibert, *Acta Chem. Scand.*, **27**, 15 (1973). <sup>z</sup> C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *J. Am. Chem. Soc.*, **97**, 6358 (1975). <sup>aa</sup> J. Bojes and T. Chivers, *Chem. Commun.*, 391 (1978). <sup>bb</sup> R. J. Gillespie, P. R. Ireland, and J. E. Vekris, *Can. J. Chem.*, **53**, 3147 (1975). <sup>cc</sup> B. D. Sharma and J. Donohue, *Acta Crystallogr.*, **16**, 891 (1964). <sup>dd</sup> I. Hargittai and F. C. Mijhoff, *J. Mol. Struct.*, **16**, 69 (1973). <sup>ee</sup> I. Hargittai, *Acta Chem. (Budapest)*, **59**, 351 (1969); **60**, 231 (1969).

*initio* calculations have shown<sup>10</sup> that inclusion of 3d AOs reduces the dipole moments of sulfur compounds, particularly in the case of compounds where sulfur is in a higher valence state. However, the errors for the compounds of divalent sulfur are on average somewhat greater than those for compounds containing only second-row elements, the calculated values for the former tending to be too large. This difference can again be attributed to neglect of 3d AOs in MNDO.

### Molecular Geometries

Table IV compares the geometries calculated for the compounds listed in Table II with the experimental values where these are available. While the agreement with experiment is reasonable, it is certainly inferior to that found previously for MNDO geometries of molecules containing only second-period elements.<sup>11</sup> The errors are moreover largely systematic, the lengths of CS bonds being

systematically underestimated by, on average, 0.068 Å, while those of HS bonds are likewise underestimated by 0.029 Å. MNDO also failed to reproduce the variation in the length of the SS bond in disulfides, *RSSR*, with changes in *R*. Thus the errors in the calculated lengths for the two extreme cases ( $S_2F_2$ , thiathiophthene) are especially large. Here again the errors are probably due to neglect of 3*d* AOs since this would be expected to lead to sulfur valence AOs which are too small and consequently to bonds that are too short. We were unable to eliminate this tendency by any changes in the parameters without introducing large errors elsewhere, e.g., in heats of formation. The SX bond lengths calculated for compounds containing sulfur in its higher valence states are much too large, indicating again the importance of 3*d* AOs of sulfur in such species.

In this connection it is interesting that the geometries of a number of sulfur nitrides are reproduced in a satisfactory manner, suggesting that the  $\pi$  bonds in them are essentially of  $p\pi:p\pi$  type. This conclusion is supported by the high electrical conductivity of polymeric sulfur nitride,  $(SN)_n$ . If the sulfur atoms in  $(SN)_n$  used 3*d* AOs for  $\pi$  bonding, the  $\pi$  bonds would be expected to show localization into three-atom segments.<sup>11</sup> The only structure not reproduced by MNDO is that of  $S_4N_4$  where MNDO predicts strong bonding between pairs of nitrogen atoms but none between the sulfur atoms, whereas the observed structure (x-ray) indicates bonding between sulfur atoms but none between nitrogen. Here it seems that 3*d* AOs of sulfur play a significant role because a recent *ab initio* Roothaan–Hall (RH) calculation,<sup>12</sup> including *d* AOs, suggested significant SS bonding but no NN bonding.\*

### Ionization Potentials and Heats of Formation of Cations


The first vertical ionization energies ("ionization potentials") calculated using Koopmans' theorem, together with experimental values where available, are shown in Table III. It will be seen that the MNDO values are systematically too large by ca. 1 eV. A similar error has been noted in MNDO calculations for compounds of other third-period el-

ements (Cl,<sup>4</sup> P<sup>13</sup>) and has been attributed to use of the core approximation in MNDO. The resulting neglect of interactions between the inner shell and valence shell AOs would be expected to lead to a decrease in the energy of the former, combined with a corresponding increase in the energy of the latter. Such interactions should not significantly affect the total energy or other collective properties of a molecule but they should alter the orbital energies, the effect on a given AO being greater, the greater the contribution to it by AOs of sulfur.

Similar effects should also be observed in the case of compounds of second-period elements but should be confined to their 2*s* AOs since here the core contains only the single 1*s* AO. Indeed, the calculated ionization energies from MOs constructed largely from 2*s* AOs of such elements are too large, and the greater the contributions by 2*s* AOs,<sup>2</sup> the greater the error. In the case of third-period elements *all* the valence shell AOs should be affected since here the core contains AOs of both *s*- (1*s*-, 2*s*-) and *p*- (2*p*-) type.

Table V shows heats of formation calculated for several radical cations derived by ionization of molecules listed in Table III, together with corresponding values for the adiabatic ionization energies of the latter and differences between them and the vertical values in Table II. It will be seen that the differences are small in the first four cases, as would be expected, since the ionizations are

**Table V.** MNDO calculations for radical cations.<sup>a</sup>

Molecule	$\Delta H$ (kcal/mole) Cal (exp)	Adiab. <sup>c</sup> IP Cal (eV)	IP vert. <sup>d</sup> IP adiab.
$H_2S^+$	245.7 (212)	10.58	.07
$HSCH_3^+$	226.2 (212)	10.18	.15
$S(CH_3)_2^+$	208.9 (191)	9.81	.26
$CS_2^+$	271.1 (261)	10.44	.15
$OCs^+$	217.9 (224)	10.72	.35
$H_2S_2^+$	227.5 (239)	9.83	.92
	237.5 (229)	9.00	.51

<sup>a</sup> Calculated using the half-electron approximation.

<sup>b</sup> J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Bur. Stand.*, No. 26 (1969).

<sup>c</sup> Calculated using heat of formation of parent compound from Table III.

<sup>d</sup> Vertical IPs (eV) taken from Table III.

\* Calculated Cartesian coordinates for the molecules studied here can be obtained upon request to M. J. S. Dewar.

from nonbonding sulfur lone-pair AOs of sulfur in  $\text{H}_2\text{S}$ ,  $\text{HSCH}_3$ , and  $\text{S}(\text{CH}_3)_2$ , and from an antisymmetric ( $\pi$ ) MO of  $\text{CS}_2$  which has a node at the central carbon atom and is therefore also nonbonding. The geometries calculated for these four radical cations are indeed similar to those for the parent molecules (Table III).

In the case of COS, however, the difference between the two ionization energies is considerably greater (Table V). This is due to the loss of symmetry on passing from  $\text{CS}_2$  ( $D_{\infty v}$ ) to COS ( $C_{\infty v}$ ). As a result, the node of the HOMO is no longer at the central carbon atom but between carbon and oxygen. Removal of an electron from this MO should therefore strengthen the CO bond and weaken the CS one, an effect shown clearly by comparison of the calculated bond lengths in the ion (CO, 1.151 Å; CS, 1.605 Å) with those in COS itself (CO, 1.176 Å; CS, 1.512 Å; Table V).

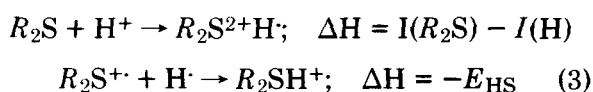
The changes in geometry are also large, and so also the corresponding differences between the vertical and adiabatic ionization energies, in the case of  $\text{H}_2\text{S}_2$  and thiophene.

In  $\text{H}_2\text{S}_2$ , the HOMO is an antibonding combination of sulfur  $3p$  AOs and is doubly occupied. For this reason the parent molecule is nonplanar, the HSSH dihedral angle being  $90.5^\circ$  (MNDO,  $99.5^\circ$ ). Removal of an electron leaves the antibonding  $\pi$  MO, derived from the sulfur  $3p$  AOs, singly occupied, while the corresponding bonding  $\pi$  MO is still doubly occupied. The net interaction in the resulting cation is therefore bonding; indeed, MNDO predicts the ion to have a *trans* planar geometry. The *trans* structure is preferred because of the repulsion between the other two lone-pair AOs of the sulfur atoms.

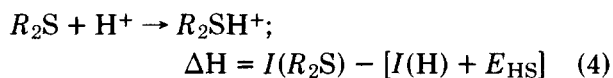
In thiophene, the HOMO is an MO symmetric for  $C_2$  rotation and therefore vanishes at sulfur, with a node between  $C_3$  and  $C_4$ . Removal of an electron from it should therefore weaken the  $C_2C_3$  and  $C_4C_5$  bonds, strengthen  $C_3C_4$ , and leave CS unchanged. The calculated bond lengths in thiophene and thiophene radical cation follow this pattern, their values (Å), with those of the ion in parentheses, being:

$$\begin{aligned} C_2C_3, 1.368 (1.429); \quad C_3C_4, 1.456 (1.404); \\ CS, 1.692 (1.686) \end{aligned} \quad (2)$$

The energetics of protonation of  $R_2S$  can be estimated by dissecting it into steps;



where  $I(R_2S)$ ,  $I(H)$  are the ionization potentials of  $R_2S$  and H and  $E_{HS}$  is the HS bond energy. Hence:



Since the bond energies of single covalent bonds are relatively constant, changes in the ionization potential of  $R_2S$  should then be reflected in its proton affinity. Since MNDO overestimates such ionization potentials by ca. 1 eV, the calculated heats of formation of the resulting cations should be too positive by the same amount. A similar analysis shows that the same should be true for cations of the type  $RS^+$ . Heats of formation calculated by MNDO for various ions of both kinds are compared with experiment in Table VI. It will be seen that, with the two exceptions, the values in Table III are systematically too large and the average deviation (23.6 kcal/mol) is nearly the same as that (19.0 kcal/mol) for the "normal" radical cations.

According to MNDO, the ion  $\text{CH}_3\text{S}^+$  is unstable, rearranging<sup>15</sup> without activation to  $\text{CH}_2=\text{SH}^+$ . The observed heat of formation for  $(\text{CH}_3\text{S})^+$  was derived from appearance potentials for its generation from precursors of the type  $\text{CH}_3\text{SX}$ . Here the ion is produced by fission of the SX bond which would normally lead to the isomer  $\text{CH}_3\text{S}^+$ . Even if bond fission is assisted by a concerted rearrangement to the more stable isomer  $\text{CH}_2=\text{SH}^+$ , the energy required should still be greater than that corresponding to formation of the latter directly. The observed appearance potential should therefore be between the values corresponding to formation of  $\text{CH}_3\text{S}^+$  and  $\text{CH}_2=\text{SH}^+$ . Although  $\text{CH}_3\text{S}^+$  is not a minimum on the MNDO potential surface, we were able to estimate its heat of formation by enforcing  $C_{3v}$  symmetry. The value found in this way was 50.5 kcal/mol greater than that for  $\text{CH}_2=\text{SH}^+$ , so the "observed" heat of formation would be expected to be too positive by roughly one-half this amount, i.e., ca. 1 eV. The true heat of formation should then be ca. 1 eV more negative than the "experimental" value listed in Table IV and so also ca. 1 eV more negative than the MNDO estimate.

A similar situation holds in the case of  $\text{PhS}^+$ , which was likewise generated from compounds of the type  $\text{PhSX}$ . Here, resonance interactions between sulfur and the ring should tend to enforce a planar geometry, so fission of the SX bond should lead initially to an ion  $\text{PhS}^+$  in which the

**Table VI.** Sulfur cations.

Molecule	Heat of Formation (kcal/mole)		Difference
	Calc. <sup>a</sup>	Obs. <sup>b</sup>	
HS <sup>+</sup> T <sub>1</sub>	298.6	274	24.6
H <sub>3</sub> S <sup>+</sup>	212.2	191	21.2
HCS <sup>+</sup>	251.7		
HSCH <sub>2</sub> <sup>+</sup>	221.0	220	1.0
H <sub>2</sub> SCH <sub>3</sub> <sup>+</sup>	197.7	174	23.7
HS(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	184.0	160	24.0
H <sub>2</sub> SSH <sup>+</sup>	216.2		
PhS <sup>+</sup>	248.9	250	-1.1

<sup>a</sup> Calculated by the half-electron version of MNDO.<sup>b</sup> H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *Energetics of Gaseous Ions*, American Chemical Society, Washington, DC, 1977.

LUMO is of  $\sigma$  type, being predominantly in the ring-sulfur plane. The most stable form of the ion will, however, be one in which the LUMO is of  $\pi$  type, corresponding to an empty  $3p$  AO of sulfur interacting with the  $\pi$  electrons of the phenyl group. In a single-configuration description, these two structures are orbital isomers<sup>16</sup> and their interconversion is "forbidden." The energy required to break the SX bond in PhSX with production of PhS<sup>+</sup> should then again be greater than that required to generate PhS<sup>+</sup> in its lowest energy state and the "experimental" heat of formation in Table IV should be correspondingly too positive.

### Higher Ionization Energies

Previous articles of this series<sup>3-7</sup> have drawn attention to a remarkable feature of MNDO, i.e., its ability to reproduce *all* the vertical ionization energies of molecules, in the correct order and with approximately correct values, assuming Koopmans' theorem. Other semiempirical methods have proved unsatisfactory in this respect, even SPINDO, which was parametrized for this specific purpose, while the RH method gives orbital energies that are uniformly greater than the observed ionization energies and are not always in the right order (e.g., F<sub>2</sub> and N<sub>2</sub>). Table VII compares MNDO orbital

energies for a number of sulfur-containing molecules with vertical ionization energies derived from photoelectron spectroscopy (PES) and with *ab initio* orbital energies. It will be seen that the MNDO and *ab initio* assignments agree in almost all cases, the few exceptions involving inversions of pairs of orbitals with similar energies.

The numerical agreement between the MNDO and *ab initio* values is quite reasonable. The MNDO ones are, however, systematically too large by ca. 1.2 eV, for reasons discussed in the previous section. If a corresponding correction is made, the MNDO values then agree well with experiment. Since the correction in the case of a given MO should be proportional to the contributions to it by AOs of sulfur, even better agreement could probably be obtained by using a correspondingly variable correction. The uncorrected MNDO values are, however, good enough to be of value in the interpretation of PES spectra.

### Barriers to Rotation About SS Bonds

As noted above, disulfides of the type RSSR have nonplanar structures and are therefore chiral. A number of investigators have studied the barriers to interconversion of the corresponding enantiomers. For dimethyl disulfide, values between

**Table VII.** MNDO higher ionization potentials.<sup>a</sup>

Molecule	Point Group	Assignment <sup>b</sup>	MNDO	Exp. <sup>c</sup>	Ab Initio
HSSH	C <sub>2</sub>	b(a) <sup>e</sup>	10.75	10.01 <sup>d</sup>	10.64 <sup>d</sup>
		a(b) <sup>e</sup>	11.12	10.28	10.54
		a	13.66	12.62	12.83
		b	15.49	14.02	15.07
		a	16.25	15.2	15.88
		b	23.01		24.35
ClSSCl	C <sub>2</sub>	a	11.45	(10.1) <sup>d</sup>	11.02 <sup>d</sup>
		b	11.45	(10.3)	11.30
		a	12.60	11.43	12.32
		b	13.86	12.20	13.59
		a	14.35	12.52	14.05
		b	14.39	(12.6)	14.13
		a	15.83	14.07	15.88
		b	16.62	15.65	16.05
		a	17.95	(17.02)	16.72
		b	23.77	(19.3)	23.29
FSSF	C <sub>2</sub>	a	11.71	10.84 <sup>d</sup>	11.93 <sup>d</sup>
		b	11.84	11.25	12.39
		a	13.41	12.94	13.86
		b	16.38	15.11	16.91
		a	16.74	15.6	18.55
		b	16.74	(16.0)	18.73
		a	17.33	(16.5)	19.3
		b	17.49	17.26	19.35
		a	18.73	(18.0)	19.90
		b	23.76	(20.0)	24.55
CH <sub>3</sub> SSCH <sub>3</sub>	C <sub>2</sub>	b(a) <sup>e</sup>	10.19	9.01 <sup>f</sup>	
		a(b) <sup>e</sup>	10.69	9.28	
		a	12.41	11.30	
		b	13.91	12.32	
		a	14.06	13.5	
		b	14.72		
		b	15.17		
		a	15.24	14.8	
		a	16.11		
		b	21.37	18.3	
HSH	C <sub>2v</sub>	b <sub>1</sub>	10.65	10.43 <sup>g</sup>	10.50 <sup>h</sup>
		a <sub>1</sub>	13.88	12.76	13.66
		b <sub>2</sub>	15.73	14.91	16.21
CH <sub>3</sub> SCH <sub>3</sub>	C <sub>2v</sub>	b <sub>1</sub>	10.07	8.68 <sup>v</sup>	9.03 <sup>v</sup>
		a <sub>1</sub>	12.20	11.35	11.30
		b <sub>2</sub>	13.32	12.75	13.29

Table VII (continued from previous page)




Molecule	Point Group	Assignment <sup>b</sup>	MNDO	Exp. <sup>c</sup>	Ab Initio
		a <sub>2</sub>	14.34	14.25	15.39
		b <sub>2</sub>	15.26	14.90	15.63
		a <sub>1</sub>	15.17	15.5	16.44
		b <sub>1</sub>	15.32	15.5	16.44
ClSCl	C <sub>2v</sub>	b <sub>1</sub>	11.04	9.67 <sup>j</sup>	10.03 <sup>j</sup>
		b <sub>2</sub> (a <sub>1</sub> ) <sup>e</sup>	13.33	12.19	12.75
		a <sub>1</sub> (b <sub>2</sub> ) <sup>e</sup>	13.39	12.19	12.69
		a <sub>2</sub>	13.73	12.45	13.41
		b <sub>1</sub>	15.25	13.91	15.37
		a <sub>1</sub>	16.20	14.67	15.63
		b <sub>2</sub>	17.85	15.70	16.49
		a <sub>1</sub>	24.78	21.0	24.34
CNSCN	C <sub>2v</sub>	b <sub>1</sub>	11.41	11.32 <sup>k</sup>	11.61 <sup>k</sup>
		a <sub>1</sub> (b <sub>2</sub> ) <sup>e</sup>	13.83	13.2	14.18
		b <sub>2</sub> (a <sub>1</sub> ) <sup>e</sup>	13.93	13.59	13.99
		a <sub>2</sub>	14.27	14.22	14.58
		a <sub>1</sub> (b <sub>2</sub> ) <sup>e</sup>	15.21	14.02	16.34
		b <sub>2</sub> (a <sub>1</sub> ) <sup>e</sup>	15.22	15.02	16.33
		b <sub>1</sub>	15.57	16.5	16.40
		a <sub>1</sub>	18.41	19.7	18.15
		b <sub>2</sub>	22.29	23.	22.28
		a <sub>1</sub>	29.10		31.04
	C <sub>2v</sub>	b <sub>2</sub>	9.98	9.38 <sup>l</sup>	9.44 <sup>l</sup>
		b <sub>1</sub>	11.82	11.76	11.25
		a <sub>1</sub>	14.39	13.85	14.62
	C <sub>2v</sub>	b <sub>2</sub>	15.99	15.20	17.40
		a <sub>1</sub>	21.52	19.9	21.97
		a <sub>1</sub>	32.06		
	C <sub>2v</sub>	b <sub>1</sub>	9.23	8.89 <sup>m</sup>	8.98 <sup>m</sup>
		b <sub>2</sub>	11.68	11.32	11.44
		b <sub>1</sub>	13.15	12.14	13.65
		a <sub>1</sub>	15.19	14.55	15.92
		b <sub>2</sub>	15.61	(15.5)	17.03
		a <sub>1</sub>	19.05	(17.2)	19.49
CH <sub>3</sub> SH	C <sub>sv</sub>	a''	10.33	9.42 <sup>i</sup>	
		a'	12.87	12.0	
		a'	14.02	13.9	
		a''	14.94	15.0	
		a'	16.01	15.5 <sup>n</sup>	

Table VII (continued from previous page)

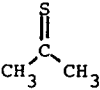

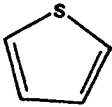
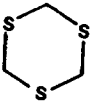
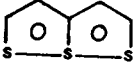
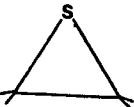
Molecule	Point Group	Assignment <sup>b</sup>	MNDO	Exp. <sup>c</sup>	Ab Initio
	C <sub>2v</sub>	b <sub>2</sub>	9.78	8.60 <sup>o</sup>	
		b <sub>1</sub>	11.07	10.46	
		a <sub>1</sub>	13.24	12.40	
	C <sub>2v</sub>	a'	9.87	8.98 <sup>o</sup>	
		a''	11.41	10.87	
		a'	13.45	12.74	
	C <sub>2v</sub>	a <sub>2</sub>	9.51	8.9 <sup>p</sup>	9.03 <sup>q</sup>
		b <sub>1</sub>	9.95	9.5	9.31
		a <sub>1</sub>	12.83	12.1	12.92
		b <sub>1</sub> <sup>r</sup>	13.29	12.7	14.26
		b <sub>2</sub>	13.79	13.3	14.23
		a <sub>1</sub>	13.88	13.9	14.69
		b <sub>2</sub>	14.39	14.3	15.86
		a <sub>1</sub>	17.37	16.6	19.10
		b <sub>2</sub>	20.69	17.6	20.41
		a <sub>1</sub>	20.96	18.3	20.73
		a <sub>1</sub>	27.05	22.1	26.83
		b <sub>2</sub>	31.16	22.3	27.07
		a <sub>1</sub>	40.44	~ 28	
	C <sub>3v</sub>	e	10.58 <sup>s</sup>	8.83 <sup>o</sup>	
		a <sub>1</sub>	10.53 <sup>s</sup>	9.27	
		e	12.65	11.22	
		e	14.08	13.07	
		a <sub>1</sub>	15.27	14.91	
		a <sub>2</sub>	15.92	16.06	
	C <sub>2v</sub>	a <sub>2</sub>	9.11 π	8.11 <sup>t</sup> σ	
		b <sub>2</sub>	9.43 σ	8.27 π	
		b <sub>1</sub>	10.62 π	9.58 π	
		b <sub>1</sub>	11.17 π	10.01 π	
		a <sub>2</sub>	12.43 π	10.64 σ	
		b <sub>1</sub>	13.29 σ	11.10 π	
S <sub>8</sub>	D <sub>4d</sub>	a <sub>1</sub> (e <sub>3</sub> ) <sup>e</sup>	11.02	9.23 <sup>u</sup>	
		e <sub>3</sub> (e <sub>2</sub> ) <sup>e</sup>	11.21		
		e <sub>2</sub> (b <sub>2</sub> ) <sup>e</sup>	11.66	9.47	
		e <sub>1</sub> (e <sub>1</sub> ) <sup>e</sup>	12.14	9.83	
		b <sub>2</sub> (a <sub>1</sub> ) <sup>e</sup>	13.04	10.12	



Table VII (continued from previous page)

Molecule	Point Group	Assignment <sup>b</sup>	MNDO	Exp. <sup>c</sup>	Ab Initio
	$C_{2v}$	$e_1$	14.60	11.35	
		$e_2$	15.40	12.54	
		$a_1$	15.76	13.47	
		$b_1$	17.20	14.08	
		$e_3$	17.30		
		$b_1$	10.17	9.03 <sup>v</sup>	9.36 <sup>v</sup>
		$b_2$	12.40	11.37	11.51
		$a_1$	12.26	11.93	11.71
		$a_2$	13.77	13.51	14.91
		$a_1$	15.66	15.33	16.43
HSCH <sub>2</sub> SH	$C_2$	$b_1$	16.62	16.58	18.50
		$b$	10.47	9.42 <sup>w</sup>	
		$a$	10.76	10.49	
		$b$	12.80	11.90	
		$a$	14.43	13.40	
OCS	$C_{\infty v}$	$\pi$	11.07	11.17 <sup>x</sup>	
		$\pi$	16.96	15.08	
		$\Sigma^+$	16.50	16.04	
		$\Sigma^+$	20.31	17.96	
		$\pi_g$	10.59	10.07 <sup>y</sup>	
CS <sub>2</sub>	$D_{\infty h}$	$\pi_a$	14.38	12.69	
		$\Sigma_u^+$	15.36	14.47	
		$\Sigma_g^+$	18.83	16.18	
		$b_{2g}$	10.95	10.52 <sup>z</sup>	10.81 <sup>aa</sup>
		$b_{3g}$	11.48	10.86	10.62
S <sub>2</sub> N <sub>2</sub>	$D_{2h}$	$b_{3u}$	11.94	11.05	12.53
		$b_{2u}$	14.01	12.30	12.94
		$a_g$	15.48	14.4	17.17
		$b_{1u}$	16.05		17.16
		$b_{1g}$	18.46		18.34
		$a_g$	21.17		19.40

6.8 and 12.3 kcal/mol have been obtained by various experimental procedures<sup>17</sup> while analysis of the rotational spectrum of H<sub>2</sub>S<sub>2</sub> led to an estimated barrier of 7.0 kcal/mol. Variable-temperature NMR studies have led to the conclusion that rotation occurs more easily via the *cis* planar rotamer rather than *trans* but this conclusion has

been contradicted by a variety of theoretical calculations.<sup>17,18</sup> The latter unanimously predict the *trans* planar isomer to be the lower in energy, estimates of the corresponding barrier to rotation varying from 0.8–14.5 kcal/mol.

Table VIII shows the results of detailed MNDO studies of the interconversion of enantiomeric

**Table VIII.** Rotational barriers.

	HSSH	FSSF	CLSSCl	CH <sub>3</sub> SSCH <sub>3</sub>	NCSSCN
Optimized Dihedral Angle	99.5	87.9	90.8	105.2	93.4
Experimental Dihedral Angle	90.5	87.9	82.5	84.7	
Trans Barrier (kcal/mole)	1.9	6.5	6.6	1.6	2.8
Cis Barrier (kcal/mole)	5.3	6.3	9.3	6.7	5.6
Experimental Barrier (kcal/mole)	7.0 <sup>a</sup>			6.8-12.3 <sup>b</sup>	

<sup>a</sup> W. N. Hubbard, D. R. Donslin, J. P. McCullough, D. W. Scott, J. F. Messerley, I. A. Hossenlopp, A. George, and A. Waddington, *J. Am. Chem. Soc.*, **80**, 3547 (1958); M. Z. El-Sabban and D. W. Scott, *U.S. Bur. Mines, Bull. No. 654* (1970).

<sup>b</sup> See references, in N. L. Allinger, M. J. Hickey, and J. Kao, *J. Am. Chem. Soc.*, **98**, 2741 (1976).

disulfides, *RSSR*, where *R* = H, F, Cl, CH<sub>3</sub>, or CN. All geometries were of course completely optimized. It will be seen that MNDO, in agreement with other theoretical procedures, predicts the *trans* barrier to be the lower in each case, except for FSSF where the *cis* barrier is lower by 0.2

kcal/mol. The MNDO values are too low, indicating that MNDO underestimates the repulsive interactions between the sulfur lone pairs, a conclusion supported by the fact that it also gives *RSSR* dihedral angles that are mostly too large.

#### Footnotes to Table VII

<sup>a</sup> Calculated via Koopmans' theorem. <sup>b</sup> Assignments follow MINDO ordering unless noted. <sup>c</sup> Vertical ionization potentials from UV-photoelectron spectroscopy. <sup>d</sup> B. Solouki and H. Bock, *Inorg. Chem.*, **16**, 665 (1977). <sup>e</sup> Original assignments ( ). <sup>f</sup> R. J. Colton and J. W. Rabalais, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 345 (1974). <sup>g</sup> G. Wagner and H. Bock, *Chem. Ber.*, **107**, 68 (1974). <sup>h</sup> M. F. Guest and W. R. Rodwell, *Mol. Phys.*, **32**, 1075 (1976). <sup>i</sup> D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell, and R. A. McLean, *J. Phys. Chem.*, **76**, 1030 (1972). <sup>j</sup> E. Solouki, P. Rosmus, and H. Bock, *Chem. Phys. Lett.*, **26**, 20 (1974). <sup>k</sup> P. Rosmus, H. Stafast, and H. Bock, *Chem. Phys. Lett.*, **34**, 275 (1975). <sup>l</sup> B. Solouki, P. Rosmus, and H. Bock, *J. Am. Chem. Soc.*, **98**, 6054 (1976). <sup>m</sup> H. Hock, B. Solouki, G. Bert, and P. Rosmus, *J. Am. Chem. Soc.*, **99**, 1633 (1977). <sup>n</sup> Original assignment made as a "corrected to a" by MNDO. <sup>o</sup> H. W. Korto, B. M. Landsberg, R. J. Suffolk, and A. Vodden, *Chem. Phys. Lett.*, **29**, 265 (1974). <sup>p</sup> P. J. Derrick, L. Åsbrink, O. Edqvist, Ö. Jonsson, and E. Lindholm, *Int. J. Mass. Spectrosc. Ion Phys.*, **6**, 177 (1971). <sup>q</sup> U. Gelius, B.

Roose, and P. Siegbahn, *Theor. Chim. Acta (Berlin)*, **27**, 171 (1972). <sup>r</sup> The *b*<sub>1</sub> orbital (MNDO, 13.29) is the third orbital in ref. p, fifth in ref. q, and fourth in MNDO. <sup>s</sup> Experimental ordering indicates e, a<sub>1</sub> sequence which is opposite MNDO sequence of a<sub>1</sub>, e. <sup>t</sup> R. Gleiter, V. Hornung, B. Lindberg, S. Hoeberg, and N. Lozac'h, *Chem. Phys. Lett.*, **11**, 401 (1971). <sup>u</sup> R. Boschi and W. Schmidt, *Inorg. Nucl. Chem. Lett.*, **9**, 643 (1973). <sup>v</sup> D. H. Aue, H. M. Webb, W. R. Davidson, M. Vidal, M. T. Bowers, H. Goldwhite, L. E. Vertal, J. E. Douglas, P. E. Kollman, and G. L. Kenyon, *J. Am. Chem. Soc.*, **102**, 5151 (1980). <sup>w</sup> C. Guimon, M. Guimon, and G. Pfister-Guillouzo, *Tetrahedron Lett.*, 1413 (1975). <sup>x</sup> P. J. Delwiche, M.-J. Hubin-Franskin, G. Caprace, P. Natalis, and D. J. Roy, *Electron Spectrosc. Relat. Phenom.*, **21**, 205 (1980). <sup>y</sup> M.-J. Hubin-Franskin, J. Delwiche, P. Natalis, and G. Caprace, *J. Electron Spectrosc. Relat. Phenom.*, **18**, 295 (1980). <sup>z</sup> D. C. Frost, M. R. Legeyt, N. Paddock, and N. P. C. Westwood, *Chem. Commun.*, 217 (1977). <sup>aa</sup> W. Von Niessen and G. H. F. Diercks, *J. Electron Spectrosc. Relat. Phenom.*, **20**, 95 (1980).

**Table IX.** Singlet-triplet splitting.

Molecule	Heats of Formation <sup>a</sup>		Singlet-triplet Splitting <sup>a</sup>	
	S <sub>0</sub>	T <sub>1</sub>	MNDO	OBS.
OS	32.2	10.3	21.9	18.16 <sup>b</sup>
S <sub>2</sub>	44.4	24.9	19.5	14.30 <sup>b</sup>
SC	96.3	147.7	51.4	
SSi	.9	78.3	77.4	70.3 <sup>c</sup>
HS+	298.6	273.9	24.7	26.8 <sup>d</sup>
S	78.8 <sup>a</sup>	57.3 <sup>e</sup>	21.5	26.4 <sup>f</sup>

<sup>a</sup> Calculated using unrestricted HF version, values in kcal/mol.<sup>b</sup> *Sulfur in Organic and Inorganic Chemistry* Vol. II, A. Senning, Ed., Marcel Dekker, New York, 1972, Chap. 12.<sup>c</sup> C. Linton, *J. Mol. Spectrosc.*, in press. Referenced by J. B. Robbe, H. Lefebvre-Brion, and R. A. Gottscho, *J. Mol. Spectrosc.*, **85**, 215 (1981).<sup>d</sup> P. E. Cade, *Can. J. Phys.*, **46**, 1989 (1968).<sup>e</sup> Fixed in MNDO as standard state of sulfur.<sup>f</sup> O. P. Strausz, R. K. Gosari, A. S. Denes, and I. G. Csizmadia, *Theor. Chim. Acta (Berlin)*, **26**, 367 (1972).

### Singlet-Triplet Splittings

Table IX shows calculated heats of formation for the lowest singlet ( $S_0$ ) and triplet ( $T_1$ ) states of several sulfur-containing molecules. The values for the triplets were calculated by the "half-electron" method.<sup>19</sup> SO, S<sub>2</sub>, HS<sup>+</sup>, and S are predicted to have triplet ground states, in agreement with experiment and as expected by analogy with O<sub>2</sub>, HN, and O. The calculated singlet-triplet separations are, moreover, in good agreement with those observed (Table VIII). This is in contrast to results obtained previously which seemed to indicate the MNDO usually underestimates the stabilities of triplets by 10–20 kcal/mol.<sup>20</sup>

Both CS and SiS are predicted to have singlet ground states, in agreement with experiment and as expected from analogy with CO. As likewise expected on this basis, the  $S_0$ - $T_1$  splittings here are very large.

**Table X.** Calculated bond strengths (kcal/mol).

	Heats of formation <sup>a</sup>				Bond Strengths <sup>a</sup>	
	XSSX	•X	•SSX	•SX	XSSX → •X + •SSX	XSSX → XS + •SX
X = H	.7	52.1	21.8	36.2	73.2	71.7
X=CH <sub>3</sub>	-18.9	25.8	12.4	21.8	57.1	62.5

<sup>a</sup> In kcal/mol.

## Strengths of SS Bonds

Table X shows CS and SS bond strengths calculated for HSSH and  $\text{CH}_3\text{SSCH}_3$ , using data from Table II together with an additional value for HS radical. MNDO correctly predicts the HS bond in HSSH to be stronger than SS, thermolysis of HSSH giving two HS radicals rather than HSS and a hydrogen atom. However, it unexpectedly predicts the reverse to be true for  $\text{CH}_3\text{SSCH}_3$ , the CS bond here being *weaker* than SS. It has been generally assumed that disulfides always undergo scission at the SS bond. At the same time, the bond strength is less than that in  $\text{H}_2\text{S}$  (observed, 91.6 kcal/mol, using data from Tables II, IX).

A similar though larger difference is observed between the HO bond strengths in  $\text{H}_2\text{O}_2$  (89.7 kcal/mol<sup>2+</sup>) and  $\text{H}_2\text{O}$  (119.2 kcal/mol\*) and is usually attributed to the presence of a three-center  $\pi$  bond in HOO, the repulsion between the oxygen lone pairs being reduced by removal of one of the lone-pair electrons. A similar effect should operate in the case of HSS<sup>+</sup> but should be smaller, because sulfur forms weaker  $\pi$  bonds than does oxygen.

MNDO predicts the SS bond in  $\text{CH}_3\text{SSCH}_3$  to be weaker than that in HSSH, as would be expected from analogy with the OO bond strengths in  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOCH}_3$  (51.5 and 29 kcal/mol, respectively\*). The experimental values imply, however, that the reverse is the case, the SS bond in  $\text{CH}_3\text{SSCH}_3$  being stronger by nearly 9 kcal/mol. This lends weight to a further, and very surprising, prediction by MNDO: the CS bond in  $\text{CH}_3\text{SSCH}_3$  is *weaker* than SS. It has always been assumed, though, to our knowledge, without definite evidence, that disulfides invariably undergo thermal scission between the sulfur atoms. It is true that the MNDO heat of formation for  $\text{CH}_3\text{SS}^\cdot$  is probably too negative, but then so is the value for  $\text{CH}_3\text{SSCH}_3$ . If the experimental value for the SS bond strength is correct, the conclusion that it is stronger than CS stands, unless the MNDO heat of formation for  $\text{CH}_3\text{SS}^\cdot$  is too low by more than 15 kcal/mol.

It has recently been shown<sup>21</sup> that the HS bonds in mercaptans are weaker than in  $\text{H}_2\text{S}$ , the difference between the values for  $\text{H}_2\text{S}$  and  $\text{CH}_3\text{SH}$  being 4.8 kcal/mol. Therefore, while MNDO underestimates the absolute strengths of these bonds, it reproduces the difference between them very well (calculated: 4.2 kcal/mol).

## CONCLUSIONS

The results reported here suggest that MNDO should be useful in interpreting the chemistry of sulfur in its "normal" valence state ( $\text{S}^{\text{II}}$ ), even without inclusion of 3d AOs. Sulfur in its higher valence states ( $\text{S}^{\text{IV}}$ ,  $\text{S}^{\text{VI}}$ ) is much too unstable, indicating the necessity of including *d* orbitals. The inclusion of *d* orbitals in the MNDO framework is currently under way in these laboratories.

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\* Using data from ref. 2.