

An Improved Set of MNDO Parameters for Sulfur

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The MNDO parameters for sulfur have been reoptimized. Calculations for a number of sulfur compounds indicate a very significant improvement. Inclusion of *d* AOs failed to correct the errors for compounds of sulfur in its higher valence states. Since *d* AOs are not included, the calculations are still confined to compounds of divalent sulfur.

INTRODUCTION

The MNDO method has been described in detail² and MNDO parameters for sulfur have been reported by Dewar and McKee.^{3,4} Use of these led, however, to unsatisfactory results in various cases, in particular for compounds containing sulfur in its higher valence states and for compounds containing sulfur-sulfur bonds. The heats of formation predicted for S^{IV} or S^{VI} compounds were too positive by very large amounts (>100 kcal/mol) while those for compounds containing S-S bonds were much too negative.

It was assumed, following convention, that the former error was due simply to the neglect of *d* AOs in MNDO. A version of MNDO was therefore developed in which *d* AOs were included.⁵ Attempts to parametrize this for sulfur were, however, unsuccessful. While the errors for compounds of S^{IV} and S^{VI} could be reduced, as would be expected in view of the additional adjustable parameters involved, the errors remained unacceptably large. We now believe that the problem lies primarily not in the neglect of *d* AOs in MNDO but in failure to allow for the contraction of AOs with positive charge. While MNDO has proved successful in calculations for numerous cations, these have not involved atoms with large formal charges, such as those present in S^{IV} or S^{VI} . While encouraging results have been obtained in a preliminary treatment⁵ where the parameters for the *d* AOs were allowed to vary with the formal charge on sulfur, problems arose in the calculation of derivatives of the energy, needed for

geometry optimization.⁶ It is also not clear that satisfactory results might not be obtained without inclusion of *d* AOs by a similar variation of the parameters for the sulfur 3*s* and 3*p* AOs. In the meantime, an improved set of conventional parameters for sulfur have been developed which in particular seem to have solved the problem concerning SS bonds. In view of current interest in sulfur chemistry in general and sulfur polymers and copolymers in particular, and since the time required to develop a comprehensive treatment of sulfur, including its higher valence states, cannot be predicted, we are now reporting the new parameters. We believe them to represent the best that can be achieved within the normal MNDO framework.

The new parameters were obtained as before, by a least squares fit to the observed properties of a selected basis set of molecules.³ The program for carrying out this optimization has been greatly improved⁷ by introduction of analytical derivatives of the various properties (heats of formation, dipole

Table I. Optimized MNDO Parameters for Sulfur.


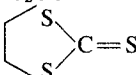
Parameter	Value	Parameter ^a	Value
U_{ss}/eV	-72.242281	DD/au	0.9189935
Z_s/au	2.312962	QQ/au	0.8328514
B_s/eV	-10.761670	AM/au	0.4733554
U_{pp}/eV	-56.973207	AD/au	0.5544502
Z_p/au	2.009146	AQ/au	0.5585244
B_p/eV	-10.108433	EISOL/eV	-226.01239
$A/\text{\AA}^{-1}$	2.478026		

^aDerived parameter; notation as in MOPAC.

moments, ionization potentials, etc.) with respect to the various parameters. This allows use of derivative optimization methods which greatly speeds up the optimization, enabling

use of more and larger molecules in the basis set. We were consequently able to use a basis set containing 21 molecules, as opposed to 13 in the earlier work, while at the same time

Table II. Calculated and Observed Heats of Formation.

Molecule	Heat of Formation (kcal/mole)		Obsd.	Error ^a
	This work	Ref. (4)		
H ₂ S*	3.8	1.7	-4.9 ^b	8.7
H ₂ S ₂ *	6.5	0.7	3.9 ^c	2.6
H ₂ S ₃ *	8.5	-1.7	3.6 ^f	4.9
H ₂ S ₄	10.7	-3.5	5.7 ^f	5.0
H ₂ S ₅	13.0	-5.7	8.0 ^f	5.0
MeSH*	-7.2	-8.5	-5.4 ^d	-1.8
EtSH	-13.2	-14.6	-11.0 ^d	-2.2
n-PrSH	-18.0	-19.4	-16.2 ^h	-1.8
i-PrSH	-16.0	-17.5	-18.1 ⁱ	2.1
n-BuSH	-22.7	-24.1	-21.1 ^h	-1.6
PhSH*	23.4	24.5	26.9 ^d	-3.5
Me ₂ S*	-17.0	-17.4	-8.9 ^d	-8.1
Me ₂ S ₂ *	-14.8	-18.9	-5.6 ^d	-9.2
Me ₂ S ₃	-13.2	-21.8	0.0 ^g	-13.2
HSCH ₂ CH ₂ SH	-4.0	-8.8	-2.2 ^d	-1.8
MeCOSH*	-41.2	—	-43.5 ^c	2.3
Thiirane*	18.9	13.8	19.7 ^d	-0.8
Thietane*	-5.0	-7.1	14.6 ^d	-19.6
 S*	-24.1	-24.9	-8.1 ^d	-16.0
Thiophene*	27.3	30.0	27.6 ^d	-0.3
MeNCS*	38.1	30.5	27.1 ^c	11.0
SCl ₂ *	-23.8	-20.0	-5.2 ^c	-18.6
S ₂ Cl ₂ *	-20.7	-21.1	-4.8 ^c	-15.9
SF ₂ *	-52.9	-35.9	-51.8 ^c	-1.1
S ₂ F ₂ *	-41.2	-29.9	-54.5 ^c	13.3
S ₄ *	45.8	27.6	32.7 ^f	13.1
S ₆	27.7	-0.4	24.5 ^f	3.2
S ₈ *	23.3	-13.7	24.5 ^f	-1.2
HNCS*	43.5	38.0	30.0 ^e	13.5
S ₂ (CN) ₂ *	70.7	75.9	82.3 ^d	-11.6
CS ₂	36.9	30.3	28.0 ^d	8.9
OCS	-22.9	-29.4	-33.85 ^d	11.0
Me ₂ CS	10.1	—	-8.9 ^d	19.0
	11.4	9.2	22.7 ^d	-11.3
SO ₂	4.5	27.5	-70.9 ^b	75.4
SO ₃	50.5	109.7	-94.6 ^f	145.1
SOF ₂	9.3	-13.2	-130.0 ^b	139.3
SOCl ₂	3.1	-3.1	-50.8 ^b	53.9
H ₂ SO ₄	15.2	45.2	-177.0 ^b	192.2

*Molecules which were included in the basis set.

^aErrors in the values calculated here.

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Table III. Calculated and Observed Dipole Moments (D).

Molecule	Calc.	Obs.	Error
H ₂ S	1.18	0.97 ^a	0.21
SCl ₂	1.23	0.36 ^b	0.87
Me ₂ S ₂	1.88	1.98 ^a	-0.10
MeNCS	2.80	4.03 ^a	-1.23
Thiophene	0.56	0.53 ^a	0.03
Me ₂ S	1.27	1.55 ^c	-0.28
MeSH	1.230	1.52 ^a	0.29
S ₂ F ₂	1.972	1.45 ^a	0.52

^aA. L. McClellan, *Table of Experimental Dipole Moments*, Freeman, San Francisco, 1963, Vol. 2.

^bJ. T. Murray, O. Williams, and T. L. Weatherly, *Bull. Am. Phys. Soc.* **17**, 575 HM11 (1973).

^cA. L. McClellan, *Table of Experimental Dipole Moments*, Freeman, San Francisco, 1963, Vol. 1.

excluding some of the diatomic and triatomic molecules previously included.

The new parameters for sulfur are listed in Table I. The heats of formation, dipole moments, and ionization potentials calculated for a number of molecules for which experimental data are available are compared with values derived from the previous parameters, and with experiment, in Tables II, III, and IV, respectively. Molecules included in the basis set for parametrization are indicated with as-

Table IV. Ionization Potentials (eV).

Molecule	Calc.	Obs.	Error
H ₂ S	10.00	10.43 ^a	-0.44
H ₂ S ₂	10.21	10.01 ^b	0.20
SCl ₂	10.71	9.70 ^c	1.01
S ₂ F ₂	11.18	10.84 ^b	0.34
Thiophene	9.50	8.90 ^d	0.60
Me ₂ S	9.58	8.65 ^e	0.93
MeSH	9.76	9.44 ^e	0.32
Thiirane	9.65	9.05 ^f	0.61
Me ₂ CS	9.31	8.60 ^g	0.71
S ₈	10.55	9.23 ^h	1.32

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Table V. Calculated (Observed) Molecular Geometries. Bond Lengths in Å, Angles in Degrees.

Molecule	Bond lengths (AB), bond angles (ABC), and dihedral angles (ABCD)
OCS ^a	CO 1.181 (1.176) CS 1.510 (1.559)
CS ₂ ^b	CS 1.493 (1.491)
H ₂ S ^c	HS 1.299 (1.328) HSH 97.8 (92.2)
H ₂ S ₂ ^d	SS 1.924 (2.055) SH 1.304 (1.328) HSS 101.8 (91.3) HSSH 99.7 (90.5)
S ₂ Cl ₂ ^e	ClS 1.973 (1.97) SS 1.923 (2.07) ClSS 107.6 (107.0) ClSSCl 89.8 (82.5)
SCl ₂ ^f	ClS 1.972 (2.014) ClSCl 105.9 (102.8)
Me ₂ S ₂ ^g	CSS 107.9 (102.8) CSSC 105.6 (84.7)
MeNCS ^h	SC 1.515 (1.517) CN 1.198 (1.192) NC 1.424 (1.479) NCS 180.0 (172.4) CNC 161.0 (141.6)
Thiophene ⁱ	CS 1.688 (1.714) C=C 1.370 (1.370) CC 1.448 (1.423)
Me ₂ S ^j	CS 1.723 (1.820) CSC 108.1 (105.0)
MeSH ^k	CS 1.718 (1.818) HS 1.304 (1.329) CSH 101.8 (100.3) HSCH 179.8 (180.0)
SF ₂ ^l	SF 1.573 (1.589) FSF 99.4 (98.3)
S ₈ ^m	SS 1.936 (2.048) SSS 108.2 (102.2) SSSS 98.5 (74.5)
S ₂ F ₂ ⁿ	FS 1.574 (1.635) SS 1.964 (1.888) FSS 106.4 (108.3) FSSF 88.0 (87.9)
EtSH ^o	HS 1.301 (1.352) CS 1.729 (1.810) HSC 102.0 (105.1)
S ₆ ^p	SS 1.949 (2.057) SSS 104.1 (102.2) SSSS 71.2 (74.5)

^aJ. K. G. Watson, *J. Mol. Spectrosc.* **48**, 479 (1973).

^bSee Table 2, ref. (a).

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terisks in Table II. The ionization potentials were estimated from the calculated orbital energies, using Koopmans' Theorem.

The calculated heats of formation are satisfactory, the average error (7.7 kcal/mol) for the compounds listed in Table II being only a little greater than that (ca. 6 kcal/mole²) for the "organic" elements and significantly less than that (10.6 kcal/mol) obtained for the same set of compounds using the old parameters. Values calculated with the latter are included for comparison in Table II. The greatest improvement is for compounds containing sulfur-sulfur bonds. The average error for these (8.2 kcal/mol) is now only a little greater than the overall average whereas before it was much larger. Results for a few compounds of sulfur in its higher valence states have been included to show the magnitude of the errors. Attempts to correct them led to correspondingly large errors for compounds of S^{II}.

The average errors in the dipole moments (0.20 *D*) and ionization potentials (0.62 eV) are also less than those in the earlier values. As before, the ionization potentials are consistently too large, although the magnitude of the error is smaller. This discrepancy was attributed⁴ to use of the core approximation in MNDO. Neglect of the interactions between the core and valence electrons would be expected to lead to ionization potentials which are too large.

Table V compares the calculated geometries with experiment. The agreement is not

as good for sulfur as it was for the "organic" elements.² The lengths of SH and SC bonds are underestimated, the average errors being 0.032 Å and 0.055 Å, respectively, while the corresponding error in the SS bond lengths is still greater (0.112 Å). While the values for bond angles are quite good, those for dihedral angles tend to be too large. Similar errors were obtained using the original parameters.⁴

The parameters reported here thus represent a very real improvement over those obtained previously.⁴ The properties calculated for compounds containing SS bonds, in particular the forms of elemental sulfur, are reproduced much more satisfactorily.

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