Theor Chim Acta (1994) 89: 1–12

Theoretica Chimica Acta

Comparison of methods to estimate geometric and electronic properties on sulfur containing compounds

Ibon Alkorta*

Molecular Research Institute, 845 Page Mill Road, Palo Alto, CA 94304, USA

Received September 1, 1993/Accepted January 12, 1994

Summary. The geometric and electronic properties of 22 sulfur derivatives have been calculated using semiempirical (PM3) and *ab initio* molecular orbital and local density functional (LDF) methods. The *ab initio* molecular orbital calculations have been carried out at the Hartree–Fock (HF) and second-order Moller–Plesset (MP2) level with the STO-3G*, MINI-1*, MIDI-1*, and 6-31G* basis sets.

The results show that the semiempirical method PM3 poorly describes the geometries and dipole moments of these compounds. The LDF method provides a very good description of the dipole moment; however, the bond distances predicted by this method are consistently longer than the experimental ones. Finally, the MIDI-1* and 6-31G* basis sets provide good geometrical results at the HF level but only the MIDI-1* is able to reproduce the experimental dipole moments at this level of theory. In the case of the 6-31G* basis set, the MP2 level is needed to provide good dipole moments.

Key words: Sulfur compounds – Semiempirical and *ab initio* methods – Local density functional theory

1 Introduction

It is known that it is only possible to obtain an adequate description of the geometric and electronic properties of sulfur containing compounds when supplementary *d* functions are included in the calculation [1]. This and the large number of electrons on sulfur has limited the size of the molecules which can be studied. In fact, it has only been possible to perform calculations at high theoretical levels on small molecules [2–9].

Since sulfur is commonly found in organic molecules including numerous biologically active compounds, it would be interesting to have reliable and inexpensive methods to calculate the properties of these compounds. For this reason, in this article, new methodologies such as *ab initio* local density functional theory calculations and semiempirical methods with improved parameters for this atom have been

---

* *Present address*: Instituto de Química Médica, Juan de la Cierva, 3, 28006-Madrid, Spain

Table 1. Theoretical and experimental geometries. Bond distances in angstroms and bond angles in degrees

		PM3	DMol	STO-3G*	MINI-1*	MIDI-1*	6-31G*	Exp.
SH_2	S–H	1.290	1.365	1.318[a]	1.419	1.337	1.327[b]	1.328[c]
	HSH	93.51	90.95	91.7	90.8	93.8	94.4	92.1
SO	S=O	1.461	1.527	1.472[a]	1.529	1.484	1.465[d]	1.481[e]
CS	C=S	1.447	1.550	1.494	1.570	1.524	1.520[b]	1.535[e]
H_2CS	C=S	1.539	1.613	1.551	1.630	1.598	1.597[b]	1.611[f]
CH_3SH	S–C	1.801	1.815	1.790[a]	1.863	1.832	1.817[b]	1.819[g]
	S–H	1.306	1.362	1.320	1.417	1.337	1.327	1.336
	HSC	99.9	97.5	94.4	94.6	97.5	97.9	96.5
SF_2	S–F	1.560	1.640	1.566	1.630	1.591	1.586[d]	1.589[h]
	FSF	96.53	99.07	99.00	98.6	98.4	97.9	98.2
SO_2	S=O	1.442	1.475	1.446[a]	1.472	1.433	1.414[b]	1.431[e]
	OSO	106.1	119.8	119.9	119.4	118.1	118.8	119.3
SF_4	S-Fax	1.621	1.680	1.606	1.649	1.620	1.632[b]	1.646[i]
	S-Fec	1.596	1.607	1.568	1.604	1.551	1.544	1.545
	FaxSFax	142.4	172.9	166.5	168.2	170.8	169.9	173.1
	FecSFec	121.2	100.5	108.9	105.3	101.6	102.7	101.6
F_2SO	S=O	1.467	1.455	1.446	1.461	1.427	1.409[b]	1.413[e]
	S–F	1.574	1.647	1.566	1.617	1.574	1.571	1.585
	FSO	101.0	106.6	108.2	108.0	106.6	106.7	106.82
	FSF	93.9	93.3	93.1	92.1	92.5	92.4	92.83
NSF	S≡N	1.476	1.464	1.468	1.507	1.446	1.431[b]	1.448[j]
	S–F	1.595	1.714	1.570	1.643	1.615	1.615	1.643
	NSF	107.1	118.9	114.4	113.3	113.8	114.1	116.5
$(CH_3)_2SO$	C–S	1.818	1.801	1.818	1.890	1.817	1.796	1.810[e]
	S=O	1.557	1.514	1.480	1.513	1.498	1.485	1.477
	CSC	99.4	94.8	94.7	91.9	97.0	97.7	96.4
	OSC	104.5	107.1	108.5	109.1	106.1	106.7	106.7

SO_3	S=O	1.384	1.456	1.450	1.460	1.422	1.405^b	1.420^k
F_4SO	S=O	1.401	1.437	1.456	1.459	1.423	1.404^b	1.403^l
	S–Feq	1.569	1.590	1.568	1.591	1.543	1.537	1.552
	S–Fax	1.593	1.628	1.596	1.620	1.577	1.582	1.575
	FeqSFeq	120.5	112.5	108.8	110.1	108.4	112.5	114.9
	FaxSFax	153.7	163.4	166.4	164.8	166.8	164.5	164.4
F_3SN	S–F	1.563	1.607	1.562	1.592	1.552	1.544^d	1.522^m
	S≡N	1.392	1.439	1.425	1.433	1.398	1.388	1.416
	FSN	123.5	123.5	123.0	123.4	123.3	122.9	122.2
	FSF	92.5	92.5	93.2	92.6	92.8	93.3	94.0
SO_4H_2	S=O	1.407	1.443	1.446	1.455	1.429	1.411	1.422^n
	S–O	1.668	1.610	1.620	1.638	1.588	1.571	1.574
	OSO	97.8	102.7	100.1	100.3	101.0	101.8	101.3
	O=S=O	126.0	125.2	125.5	125.2	124.1	123.7	123.3
CH_3SO_2Cl	S=O	1.423	1.454	1.450	1.461	1.433	1.418	1.424^o
	S–C	1.769	1.758	1.818	1.872	1.792	1.780	1.763
	S–Cl	2.104	2.078	2.061	2.117	2.100	2.049	2.046
	OSO	120.2	122.7	123.7	123.3	121.7	121.2	120.8
CH_2SF_4	S=C	1.496	1.584	1.572	1.629	1.572	1.567	1.554^p
	S–Fax	1.613	1.632	1.577	1.618	1.586	1.592	1.593
	S–Fec	1.584	1.610	1.590	1.599	1.560	1.560	1.560
	FaxSFax	148.9	171.5	171.8	172.4	171.8	170.7	170.5
	FecSFec	117.7	96.5	99.0	98.1	96.9	98.2	96.8
$(CH_3)_2SO_2$	S=O	1.468	1.462	1.455	1.466	1.451	1.437	1.431^q
	S–C	1.793	1.765	1.819	1.870	1.791	1.774	1.777
	CSC	100.0	107.9	99.1	97.3	103.6	104.3	103.2
	OSO	118.3	121.4	123.0	122.9	120.5	120.1	121.1

Table 1. Continued

		PM3	DMol	STO-3G*	MINI-1*	MIDI-1*	6-31G*	Exp.
$(NH_2)_2SO_2$	S=O	1.458	1.453	1.449	1.461	1.441	1.420[r]	1.429[s]
	S–N	1.746	1.650	1.705	1.739	1.663	1.640	1.620
	OSO	121.7	125.0	125.5	124.6	123.4	123.4	119.2
	NSN	101.0	107.0	101.5	101.5	105.2	106.6	111.4
	NSO	108.1	105.2	106.7	107.1	106.7	106.4	106.5
F_2SO_2	S=O	1.400	1.434	1.443	1.446	1.413	1.396	1.405[t]
	S–F	1.547	1.585	1.557	1.581	1.541	1.531	1.530
	FSF	95.3	94.8	94.9	94.46	94.9	95.2	96.1
	OSO	126.4	126.9	124.9	125.3	125.7	124.7	124.0
Cl_2SO_2	S=O	1.401	1.447	1.447	1.457	1.425	1.409	1.405[u]
	S–Cl	2.075	2.037	2.028	2.093	2.037	1.998	2.011
	OSO	122.5	124.1	124.9	124.1	123.5	122.8	123.5
	ClSCl	95.9	110.0	94.9	98.5	99.5	101.3	100.0
$CH_2CH_2SO_2$	S=O	1.441	1.464	1.458	1.471	1.448	1.433	1.439[v]
	S–C	1.762	1.745	1.758	1.822	1.746	1.725	1.731
	OSO	119.9	123.25	124.1	123.7	122.1	121.7	121.26
	CSC	51.1	53.58	52.6	52.5	53.7	54.3	54.40

[a] From Ref. [13]. [b] From Ref. [14]. [c] From Ref. [18]. [d] From Ref. [19]. [e] From Ref. [20]. [f] From Ref. [21]. [g] From Ref. [22]. [h] From Ref. [23]. [i] From Ref. [24]. [j] From Ref. [25]. [k] From Ref. [26]. [l] From Ref. [27]. [m] From Ref. [28]. [n] From Ref. [29]. [o] From Ref. [30]. [p] From Ref. [31]. [q] From Ref. [32]. [r] From Ref. [33]. [s] From Ref. [34]. [t] From Ref. [35]. [u] From Ref. [36]. [v] From Ref. [37].

studied. These methods are less time consuming than molecular orbital *ab initio* calculations and for this reason can be used for bigger systems. The results obtained by these two methods have been compared to Hartree–Fock (HF) and second-order Moller–Plesset perturbation (MP2) level *ab initio* calculations and experimental data of a set of small molecules containing sulfur in its three different oxidations states: II, IV, and VI.

Methods

The compounds studied are shown in Table 1. The molecules have been optimized retaining their characteristic symmetry. In the case of molecules with several conformational minima, the one observed experimentally has been studied.

The PM3 [10] calculations were performed using the MOPAC 6.0 package [11]. Geometry optimizations using MOPAC were performed employing the PRECISE keyword which increases the precision of the electronic and geometric parameters by two orders of magnitude. These optimized geometries have been used for the rest of the calculations, except for the cases in which published geometries were available for the same method.

The molecular orbital *ab initio* calculations were done using Gaussian 92 [12]. The structures were optimized at the HF level using the Berny method as implemented in the Gaussian 92 program. All other parameters in the optimization process were left at their default values. The standard Pople's STO-3G* [13] and 6-31G* [14] basis sets were used. Additionally, calculations with the Huzinaga's MINI-1* [15] and MIDI-1* [15] basis sets have been performed using the option of generic external basis sets. The MINI-1* is a minimal basis set similar to the STO-3G* including polarization functions over all the atoms and the MIDI-1* basis set has a similar representation to the 3-21G* with polarization, additionally, on the hydrogens. At the MP2 level [16], single point calculations have been carried out using the optimized HF/MIDI-1* and HF/6-31G* structures.

The LDF/LDA calculations were carried out using the DMol package (Version 2.2) [17], distributed by Biosym Technologies. A double numerical basis set, including polarization (DNP), was used. The keyword FINE was used for the mesh points for the numerical integration procedure involved in the evaluation of the matrix elements. The angular integration points considered spherical harmonics up to $l = 3$ for the heavy atom and $l = 2$ for the hydrogens. The optimizations were carried out until the largest component of the gradient was smaller than 1×10^{-3}.

The force constant matrix of the minimized structures with PM3 and DMol were calculated to confirm that they were true minima.

Finally, the value of the exponent of the *d* function on the sulfur was modified using the DAtom program to generate the numerical basis sets of the *d* functions corresponding to elements with atomic numbers between 12 and 18.

Results

In order to evaluate the reliability of the different methods used to predict the properties of sulfur containing compounds, geometric and electronic aspects have been studied. The bond lengths and bond angles have been studied as geometric descriptors of the molecuales and the dipole moment to evaluate the description of the electronic distribution.

Table 2. Statistical analysis of the geometrical parameters using Eq. (1)

	c	Standard deviation	r
Bond lengths ($n = 40$)[a]			
PM3	1.020	0.045	0.9717
DMol	1.020	0.022	0.9923
STO-3G*	1.007	0.033	0.9811
MINI-1*	1.033	0.026	0.9898
MIDI-1*	1.005	0.017	0.9958
6-31G*	0.997	0.012	0.9976
Bond angles ($n = 31$)[b]			
PM3	0.982	9.534	0.9184
DMol	1.006	2.694	0.9939
STO-3G*	0.999	3.595	0.9892
MINI-1*	0.996	3.222	0.9917
MIDI-1*	0.998	2.153	0.9962
6-31G*	0.999	1.688	0.9976

[a] Standard deviation in Å. [b] Standard deviation in deg

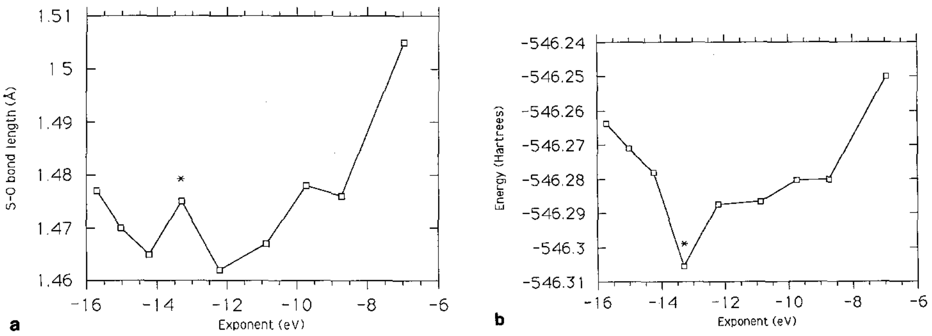

Fig. 1. Influence of the exponent of the d functions on sulfur in: (a) the SO bond distance, and (b) the total energy of SO_2. The "*" indicates the value of the standard exponent used by the DMol program

The geometrical results obtained for the molecules studied with all the methods used are shown in Table 1. In the same table, experimental values, determined with microwave spectroscopy when available, are included. A statistical analysis of these results is shown in Table 2. The analysis has been performed by a least-square fitting of the type

$$\mathrm{CALCULATED}_i = c * \mathrm{EXPERIMENTAL}_i \qquad (1)$$

for the bond distances and bond angles separately.

This analysis allows to evaluate the similarity and the possible systematic errors of the calculated results when compared with the experimental ones. The value of the slope, c, indicates the degree of similarity and the standard deviation, the average deviation of the values from the corresponding regression. Ideally a slope close to 1.0 and a very small standard deviation will be desired. However, slopes different from 1.0 can be useful if their corresponding standard deviation is small.

Table 3. Theoretical and experimental dipole moments (D)

	PM3	DMol	STO-3G*	MINI-1*	MIDI-1*	6-31G*	MP2/MIDI-1*// HF/MIDI-1*	MP2/6-31G*// HF/6-31G*	Exp
SO	1.30	1.52	1.52	1.35	1.67	1.92	1.16	1.51	1.55[a]
CS	1.42	2.15	2.13	1.39	1.49	1.34[b]	2.09	2.07	1.98[a]
H_2CS	2.07	1.54	0.10	1.09	2.08	2.24[b]	1.55	1.70	1.65[c]
SH_2	1.78	0.92	0.31	0.88	1.27	1.41[b]	1.25	1.49	0.97[a]
SF_2	0.99	1.16	0.67	1.28	1.45	1.61	1.02	1.30	1.05[d]
CH_3SH	1.95	1.50	0.40	0.96	1.65	1.79[b]	1.54	1.78	1.52[a]
SO_2	3.63	1.47	1.47	1.75	2.03	2.19[b]	1.38	1.64	1.63[e]
SF_4	2.37	0.75	0.21	0.94	0.97	1.00	0.65	0.78	0.63[f]
F_2SO	3.46	1.48	1.59	1.73	2.10	2.22	1.51	1.72	1.63[a]
NSF	2.69	1.78	1.98	1.57	1.93	2.15	2.05	2.31	1.90[g]
$(CH_3)_2SO$	4.49	3.87	2.90	3.00	4.05	4.50	3.25	3.95	3.96[a]
SO_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00[a]
F_3SN	2.59	1.33	2.47	1.43	1.94	2.27	1.80	1.98	1.91[h]
H_2SO_4	2.20	2.86	2.67	2.11	2.60	3.47	2.26	3.16	2.72[i]
$(CH_3)_2SO_2$	4.97	4.36	3.33	3.44	4.67	5.10	3.77	4.50	4.43[j]
$NH_2SO_2NH_2$	2.36	3.98	3.30	3.54	4.32	4.81	3.70	4.39	3.9[k]
F_2SO_2	1.53	0.74	1.33	0.84	1.08	1.30	0.97	1.15	1.11[l]
Cl_2SO_2	0.10	1.72	0.74	1.39	1.68	2.15	0.83	1.49	1.81[a]
$CH_2CH_2SO_2$	3.26	4.52	3.09	3.33	4.60	5.10	3.61	4.42	4.41[m]

[a] From Ref. [41]. [b] From Ref. [42]. [c] From Ref. [21]. [d] From Ref. [23]. [e] From Ref. [43]. [f] From Ref. [24]. [g] From Ref. [44]. [h] From Ref. [28]. [i] From Ref. [29]. [j] From Ref. [32]. [k] From Ref. [45]. [l] From Ref. [35]. [m] From Ref. [37].

Table 4. Statistical analysis of the dipole moments ($n = 19$) using Eq. (1)

	c	Standard deviation (D)	r
PM3	1.001	1.099	0.6757
DMol	0.984	0.194	0.9905
STO-3G*	0.783	0.558	0.8812
MINI-1*	0.804	0.268	0.9681
MIDI-1*	1.054	0.266	0.9818
6-31G*	1.180	0.315	0.9795
MP2/MIDI-1*// HF/MIDI-1*	0.870	0.283	0.9693
MP2/6-31G*// HF/6-31G*	1.050	0.228	0.9866

This will indicate a systematic error that can be eliminated by multiplying the calculated value by $1/c$.

The influence of the value of the exponent of the *d* functions on sulfur in LDF calculations on the geometry and total energy has been studied. For this purpose, the geometry (Fig. 1a) and total energy (Fig. 1b) of SO_2 has been calculated in a range of values of this exponent.

The dipole moments calculated for a selected group of molecules in which the experimental values were known are gathered in Table 3. Additionally, a statistical analysis of the results is gathered in Table 4.

Discussion

Geometry

The results obtained for the geometrical parameters (Table 2) shows that the *ab initio* methods provide reasonable geometries when compared to the experimental ones, as can be seen from the small standard deviations and slope close to 1.0.

The only semiempirical method studied, PM3, reproduced with acceptable accuracy the bond distances, as indicated by a slope close to 1.0 (1.005) and a standard deviation that is slightly larger than the one provided by the minimal basis set STO-3G*. However, the description of the bond angles is very poor and in several cases the error of the calculated value is larger than 20°. Additional problems found with this method are its poor description of different conformations of some of the molecules. One of the worst cases is sulfamide, in which the nitrogens are described as planar in contrast with the experimental and *ab initio* pyramidal disposition.

The analysis of the *ab initio* results shows that the split-valence basis sets with polarization, MIDI-1* and 6-31G*, provides the best results. Their slopes and correlation coefficients, for both bond distances and bond angles, are the ones closer to 1.0 and standard deviations which are the smallest.

The minimal basis sets, STO-3G* and MINI-1*, show different tendencies with respect to the bond distance prediction. The first basis set predicts, in general, very good bond distances (slope close to 1.0), whilst the second one has a smaller standard deviation but a worse slope. In an absolute sense, the STO-3G* give bond distances closer to the experimental ones than the MINI-1*. Both give good results with respect to bond angles.

Based on their correlation coefficient and standard deviation, the quality of the LDF results can be considered as intermediate between the ones obtained with the minimal and the split-valence basis sets studied. The calculated bond distances with this method are consistently longer than the experimental ones as shown by a slope larger than 1.0 (1.02) and a small standard deviation (0.022). A similar tendency has been reported for fluoro derivatives of xenon [38], iodine [39] and sulfur [40] calculated with this method.

Influence of the exponent of the d functions on sulfur in LDF calculations

The values of the exponent of the *d* functions on sulfur have been shown to have a large influence on the values of the bond length and total energies in molecular orbital *ab initio* calculations [33]. In this case, the geometries and total energies of the SO_2 have been calculated varying the exponent of the *d* function on the sulfur, in LDF methods, between −6.96 and −15.72 eV.

The S–O bond length variation shows a very irregular trend (Fig. 1a). The distance corresponding to the standard exponent for the sulfur is a local maximum surrounded by two minima in which the bonds have been shortened around 0.01 Å. The rest of the values of the exponent show an enlargement of these distances. This behavior contrasts with the monotonic decrease in the S–O distances as the exponent increases observed in molecular orbital *ab initio* calculations [33].

In contrast, the variation of energy with the exponent is more regular, with a deep minimum in the standard value for the sulfur. A similar tendency has been observed in molecular orbital *ab initio* calculations with the 6-31G* basis set [33].

Based on these results it is clear that a change in the value of the exponent can provide a small shortening of the bond length at the expense of a large increase in the value of the total energy.

Dipole moment

The absence of *d* functions on the sulfur has been shown to produce a zwitterionic description in hypervalent sulfur compounds. Similar problems are found in the semiempirical method PM3 that does not use *d* functions. From Table 3, it is clear that this method describes better compounds with S(II) than with S(IV) and S(VI). The description of these compounds shows a very positive charge on the sulfur, and large negative charges in the heteroatoms bonded to it. Another indication of its limitations is the bond order of almost one for double bonds. One example of this behavior is the variation in the SO bond order in the SO_n series, that changes from 1.95 for $n = 1$, 1.48 for $n = 2$, to finally 1.28 for $n = 3$. This poor electronic representation is reflected in bad dipole moments as can be seen by its small correlation with the experimental values and a large standard deviation (1.1 D).

The *ab initio* methods studied, which include additional *d* functions, give better results than PM3. However, these results can only be considered good at the HF level for the molecular orbital calculations with the MIDI-1* basis set. The minimal basis sets, STO-3G* and MINI-1*, provide, in general, dipole moments smaller than the experimental ones. A comparison of the minimal basis sets reveals that MINI-1* is superior to STO-3G*, having better correlations and smaller standard deviations from experimental values.

Surprisingly, the split-valence 6-31G* basis set at the HF level fails to predict good dipole moments, giving considerably larger values for them. The problems of this basis set do not seem to be due to the description of the sulfur since the inclusion of a second set of *d* functions on this atom improved only slightly the prediction of this property [46].

The inclusion of correlation (MP2) in the molecular orbital *ab initio* calculations reduce, in general, the value of the dipole moment when compared to the HF results. Additionally, the differences of the HF and MP2 dipole moments for each compound with the two basis sets studied, MIDI-1* and 6-31G*, are very similar. The results are consistently improved in the case of the 6-31G* basis set, whilst they are worse for the MIDI-1* basis set. This could indicate the necessity of a higher level of theory to assure a good dipole moment prediction in this kind of compounds.

The LDF results provide, in average, the best dipole moments of all the methods studied, even better than the ones obtained with the MP2/6-31G*. The good dipole moment predictions based upon the DMol calculations contrast with a recent report that indicated, for a different set of compounds, a poor performance of several LDF methods using a basis set derived from the 6-31G* basis set [47]. These results, taken together, indicate the sensibility of LDF calculations to the basis set used.

Conclusion

In this work, a comparative analysis of the performance of semiempirical and *ab initio* methods on sulfur derivatives has been carried out.

The results for the semiempirical method, PM3, show that this method poorly describes the geometric and particularly the electronic properties of these compounds.

A comparison of the results obtained with the minimal basis sets indicates that the use of STO-3G* gives better geometries than MINI-1*. Although the dipole moments of MINI-1* are somewhat better than STO-3G*, neither are particularly good.

The split-valence basis sets, MIDI-1* and 6-31G*, give accurate geometries but only the MIDI-1* predicts properly the dipole moment of the molecules at the HF level. In this study, the HF/6-31G* calculations predict very large dipole moments that are not improved significantly with the inclusion of a second set of *d* functions on the sulfur.

The inclusion of correlation (MP2) in the calculations reduces, in general, the value of the dipole moments, improving the results obtained with the 6-31* basis sets when compared to the HF level.

The LDF results indicate that this is a very good method to predict the electronic distribution of these molecules, though it consistently provides large bond distances for the atoms united to the sulfur.

In conclusion, *ab initio* LDF, and HF/MIDI-1* and MP2/6-31G* molecular orbital calculations provide the most adequate prediction of the geometric and electronic characteristics of these types of molecules.

Acknowledgement. The author thanks Dr. Danni Harris for his support and helpful comments and the Ministerio de Educación y Ciencia of Spain for financial support.

References

1. Henre WJ, Radom L, Schleyer PvR, Pople JA (1986) *Ab initio* molecular orbital theory. Wiley, New York
2. Bacskay GB, Rendell APL, Hush NS (1988) J Chem Phys 89:5721
3. Quelch GE, Schaefer III HF, Marsden CJ (1990) J Am Chem Soc 112:8719
4. Patterson CH, Messmer RP (1990) J Am Chem Soc 112:4138
5. Davy RD, Schaefer III HF (1991) J Am Chem Soc 113:1917
6. Wong MW, Wiberg KB, Frisch MJ (1992) J Am Chem Soc 114:523
7. Wong MW, Wiberg KB (1992) J Am Chem Soc 114:7527
8. Magnusson E (1993) J Am Chem Soc 115:1051
9. Magnusson E (1993) J Comp Chem 13:54 and 13:67
10. Stewart JJP (1989) J Comp Chem 10:209 and 10:221
11. Stewart JJP (1990) MOPAC 6.0, QCPE Program 455, Bloomington, IN
12. Frisch MJ, Trucks GW, Head-Gordon M, Gill PMW, Wong MW, Foresman JB, Johnson BG, Schlegel HB, Robb MA, Replogle ES, Gomperts R, Andres JL, Raghavachari K, Binkley JS, Gonzalez C, Martin RL, Fox DJ, Defrees DJ, Baker J, Stewart JJP, Pople JA (1992) Gaussian 92, Revision A. Gaussian, Inc, Pittsburgh, PA
13. Collins JB, Schleyer PvR, Binkley JS, Pople JA (1976) J Chem Phys 64:5142
14. Francl MM, Pietro J, Hehre WJ, Binkley JS, Gordon MS, DeFrees DJ, Pople JA (1982) J Chem Phys 77:3654
15. Tatewaki H, Huzinaga S (1980) J Comp Chem 1:205. Sakai Y, Tatewaki H, Huzinaga S (1981) J Comp Chem 2:108
16. Pople JA, Binkley JS, Seeger R (1976) Int J Quant Chem, Chem Symp 10:1
17. Delley B (1990) J Chem Phys 92:508
18. Allen Jr HC, Plyler EK (1956) J Chem Phys 25:1132
19. Reed AE, Schleyer PvR (1990) J Am Chem Soc 112:1434
20. Harmony MD, Laurie VW, Kuczkowski RL, Schwendeman RH, Ramsay DA, Lovas FJ, Lafferty WJ, Maki AG (1979) J Phys Chem Ref Data 8:619
21. Johnson DR, Powell FX, Kirchhoff WH (1971) J Mol Spectrosc 39:136
22. Kojima T, Nishikawa T (1957) J Phys Soc Jpn 12:680
23. Johnson DR, Powell FX (1969) Science 164:950
24. Tolles WM, Gwinn WD (1962) J Chem Phys 36:1119
25. Kirchhoff WH, Wilson Jr EB (1963) J Am Chem Soc 85:1726
26. Kaldor A, Maki AG (1973) J Mol Struct 15:123
27. Gundersen G, Hedberg K (1969) J Chem Phys 51:2500
28. Kirchhoff WH, Wilson Jr EB (1962) J Am Chem Soc 84:334
29. Kuczkowski RL, Sueram RD, Lovas FJ (1981) J Am Chem Soc 103:2561
30. Hargittai M, Hargittai I (1973) J Chem Phys 59:2513
31. Simon VA, Peters EM (1980) Z Anorg Chem 468:7
32. Saito S, Makino F (1972) Bull Chem Soc Jpn 45:92
33. Mo O, de Paz JLG, Yañez M, Alkorta I, Elguero J, Goya P, Rozas I (1989) Can J Chem 67:2227
34. Belaj F, Kratky C, Nachbaur E, Popitsch A (1987) Monatsh Chem 118:427
35. Lide Jr DR, Mann DE, Fristrom RM (1957) J Chem Phys 26:734
36. Hargittai I (1978) Sulphone molecular structures. Lecture notes in chemistry, Vol 6. Springer, Berlin
37. Nakano Y, Saito S, Morino Y (1970) Bull Chem Soc Jpn 43:368
38. Christe KO, Curtis EC, Dixon DA, Mercier HP, Sanders JCP, Schobilgen GJ (1991) J Am Chem Soc 113:3351
39. Christe KO, Curtis EC, Dixon DA (1993) J Am Chem Soc 115:1520
40. Christe KO, Dixon DA, Golberg IB, Schack CJ, Walther BW, Wang JT, Williams F (1993) J Am Chem Soc 115:1129
41. Weast RC (1980) CRC handbook of chemistry and physics, 61st ed. CRC Press, Boca Raton
42. Pietro WJ, Francl MM, Hehre WJ, DeFrees DJ, Pople JA, Binkley JS (1982) J Am Chem Soc 104:5039
43. Patel D, Margolese D, Dyke TR (1979) J Chem Phys 70:2740
44. Cook RL, Kirchhoff WH (1967) J Chem Phys 47:4521

45. Devoto G (1933) Gazz Chim Ital 63:495
46. A single point calculation with a double set of *d* functions on the sulfur and the standard 6-31G* basis set for the rest of the atoms in three molecules has provided the following dipole moments: 2.22 for SO_2, 1.22 for SH_2, and 2.02 D for F_2SO
47. Johnson BG, Gill PMW, Pople JA (1993) J Chem Phys 98:5612