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SUBSTITUENT EFFECTS IN SECOND ROW MOLECULES

SULFUR(II) COMPOUNDS

ERIC MAGNUSSON
Contribution from the Research School of Chemistry, Australian National University,
G.P.O. Box 4, Canberra, A.C.T., Australia 2601

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Abstract - Substituent effects arising from directly bonded groups in sulfur-containing compounds are investigated by molecular orbital calculations of relative energies. Interaction energies, basicities and acidities are obtained from calculations at the supplemented 4-31G and 6-31G basis set levels for substitution in the three series of sulfur compounds SX^-, SHX, and SH_2X^+ with X - BH_2, CH_3, NH_2, OH, F and in the bi-substituted series SX_2 (X - CH_3, F). Donor–acceptor interactions are dominated by the σ-electrons and readily account for the data; substitution by BH_2 is an exception, requiring consideration of π-bonding, especially in the anion. Charge transfer, both to and from the second row element, is better tolerated by the sulfur-containing systems than by the corresponding oxygen compounds.

A systematic study of the effects of substitution on the oxygen-containing series OX and OHX by Radom *et al.*[1] is here extended to the sulfur-containing species SHX, SX , and SH_2X^+ for the substituents X = BH_2, CH_3, NH_2, OH, and F. Similar studies on phosphorus and silicon compounds are reported separately.[2]

Theoretical substituent parameters recently proposed by Topsom[3] are useful as a guide to the electrostatic effects (the σ_F(theor.) parameter) and the resonance effects (the σ_R(theor.) parameter) expected for the substituents used in this study. σ_X(theor.) is a measure of group electronegativity on a scale in which the value for H is zero, and therefore gives negative values for less electronegative groups.

Group X:	BH_2	CH_3	NH_2	OH	F
σ_X(theor.)	0.09	0.17	0.33	0.43	0.52
σ_F(theor.)	0.06	−0.02	0.16	0.31	0.49
σ_R(theor.)	0.51	−0.03	−0.48	0.44	−0.34

Values of the same parameters for SH, S^-, and SH_2^+ are:

Second row centre:	SH	S^-	SH_2^+
σ_X(theor.)	0.07	−0.07	0.21
σ_F(theor.)	0.28	2.01	2.46
σ_R(theor.)	−0.21	−0.75	−0.01

These figures suggest that the SH and OH groups will display similar overall substitution behaviour across the X = BH_2, CH_3, NH_2, OH, F series, attenuated in the SHX compounds because of the reduced σ-acceptor and π-donor abilities of the second row group. By extension, the response to substitution shown by the SX and SH_2X^+ series is also expected to be milder than in the corresponding first row molecules.

METHOD OF CALCULATION AND RESULTS

MO calculations were made with the use of the Gaussian 80 series of programs.[4] The basis set variation of geometries and of energy data is discussed elsewhere[5] and argument in this paper is based on the results obtained from the supplemented 6-31G basis set, using geometries optimized at the supplemented 4-31G level.[6,7] Calculations on the anions SX^- and OX^- were repeated with the 6-31G# # and 4-31G basis sets supplemented by diffuse *s* and *p* functions, as recommended by Spitznagel *et al.*[8] Preliminary calculations were used to choose a value of *k* = 0.04 for the exponent of the additional sulfur *s* and *p* functions. The basis sets supplemented with diffuse *s* and *p* functions are designated 4-31 + G and 6-31 + G # #.

Calculated molecular energies (4-31G(#) and 6-31G # # levels)[7] and optimized geometries (4-31G(#) level) for molecules of the SX^- series are set out in Table 1 and Fig. 1 together with data for the X = BH_2 members of the SHX and SH_2X^+ series. Energy data for the remaining members of the latter series are reported in another place.[5] Interaction energies (ΔE(X, H)) and basicity and acidity data are given in Tables 2 and 3 and Fig. 2. Data from the analogous oxygen-containing systems, calculated from energy information published by Radom *et al.*, are included for comparison.[1] In the case of the anions OX , the data were obtained by calculation.

The geometrical data obtained by optimization calculations on SX^-, SHX, and SH_2X^+ series show contraction of bond distances from anionic to neutral to cationic species of some 10–20 pm for the X = CH_3, NH_2, OH, F species and a similar bond lengthening for the π-acceptor BH_2; these figures are very similar to those for the corresponding first row compounds.[1] As found for other similar main group compounds, conformations are adopted that minimize the effect of unfavourable lone pair lone pair interactions. This is not possible, of course, in the SX^- series compounds.

DISCUSSION

In their comments on the general pattern of substituent effects on first row systems, Hinde, Pross and Radom[1a] class the XOH series with XNH_2 and XF and the XO series with XNH . Except for interactions with X = BH_2, σ-electron donor–acceptor interactions are considered to dominate: because they

Table 1. Calculated total energies (Hartrees) of SX⁻ series molecules (X = H, BH$_2$, CH$_3$, NH$_2$, OH, F), SH · BH$_2$ and SH$_2$ · BH$_2^+$, and OX⁻ series molecules*

Basis Set:	4-31G(#)	6-31G##	6-31+G##		4-31+G
SH$^-$	−397.63838	−398.09588	−398.10983	OH	−75.28990
S · BH$_2$	−422.90917	−423.39114	−423.39927	O · BH$_2^-$	−100.59460
S · CH$_3$	−436.60795	−437.11781	−437.12916	O · CH$_3$	−114.25226
S · NH$_2$	−452.55257	−453.08841	−453.10811	O · NH$_2^-$	−130.18219
S · OH	−472.37096	−472.91293	−472.93651	O · OH$^-$	−149.89233
SF$^-$	−496.37258	−496.91517	−496.94203	O · F$^-$	−173.98515
SH · BH$_2$	−423.48782	−423.95515			
SH$_2$ · BH$_2^+$	−423.76434	−424.23104			

* All calculations on geometries optimized at the 4-31G(#) level (4-31G for the oxygen compounds).

are unfavourable, substituent interaction energies for the processes

$$OHX + H_2 \rightarrow OH_2 + HX$$

$$OX^- + H_2 \rightarrow OH^- + HX$$

are negative, becoming more and more so as the electronegativity of the central atom increases. Electron withdrawal from oxygen in the OX⁻ series is less unfavourable than in the neutrals, ΔE(X, H) values actually increasing for X = NH$_2$, OH, F as electron withdrawal reduces the charge on the oxygen atom. Conversely, the effect of the same substituents on the oxygen atom electron density in the cationic series OH$_2$X$^+$ produces a very steep destabilization.

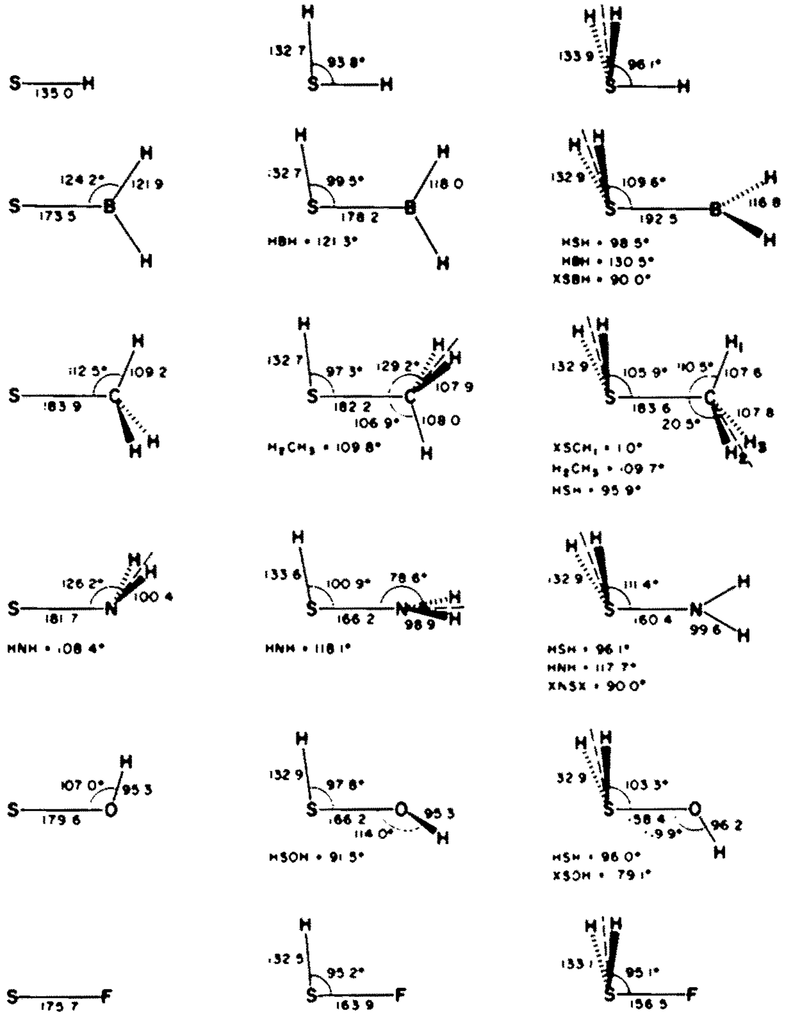

Fig. 1. Optimized geometries for SX⁻, SHX, and SH$_3$X$^+$ series molecules (X = H, BH$_2$, CH$_3$, NH$_2$, OH, F) obtained from 4-31G(#) level calculations. (Bond lengths in pm, bond angles in degrees.)

Table 2. Calculated substituent interaction energies for SX^-, SHX, and SH_2X^+ series molecules (X = BH_2, CH_3, NH_2, OH, F) with comparative data for OX^-, OHX, and OH_2X^+ series (kJ mol^{-1})[a,b]

	X =	BH_2	CH_3	NH_2	OH	F
SX	6-31 + G # #	75.1	−132.5	171.1	−168.1	−122.8
	6-31G # #	90.3	−125.6	−186.2	−193.3	−156.7
	4-31G(#)	125.8	−115.1	−156.5	−130.4	−70.1
SHX	6-31G # #	54.0	−97.6	−149.6	−177.1	−189.9
	4-31G(#)	59.1	97.5	−118.9	−154.2	−154.8
SH_2X^+	6-31G # #	49.9	−29.0	−81.3	−149.2	−219.3
	4-31G(#)	42.5	−36.3	−64.3	−150.8	−226.0
OX	4-31 + G	214.8	134.0	231.1	−235.9	−172.4
	4-31G	314.6	−64.0	−184.9	−181.2	−128.4
OHX	4-31G	118.8	−132.6	254.9	−343.9	−403.5
OH_2X^+	4-31G	126.5	−62.5	−258.4	−402.1	595.1

[a] Interaction energies refer to the reactions:

$$\begin{cases} SX^- \\ SHX \\ SH_2X^+ \end{cases} + H_2 \rightarrow \begin{cases} SH + HX \\ SH_2 \\ SH_3^+ \end{cases}$$

[b] Sulfur molecules calculations at 4-31G(#) optimized geometries. 4-31 + G results for anionic oxygen compounds are from this research, 4-31G//4-31G calculations from ref. 1.

Table 3. Calculated relative basicities and acidities for SHX series molecules (X = BH_2, CH_3, NH_2, OH, F)[a,b]

	X =	BH_2	CH_3	NH_2	OH	F
Relative basicities:						
SHX	6-31G # #	−4.1	68.6	68.3	27.9	−29.4
	4-31G(#)	−16.6	61.2	54.6	3.3	71.3
OHX	4-31G	7.7	70.1	−3.6	58.2	−191.5
Relative acidities:						
SHX	6-31 + G # #	21.1	−34.9	−21.5	9.0	67.1
	6-31G # #	36.4	−28.0	−36.6	−16.3	33.2
	4-31G(#)	66.7	−17.5	−37.6	23.7	84.6
OHX	4-31 + G	96.0	−1.37	23.8	108.1	231.2
	4-31G	194.6	67.6	68.7	161.6	274.0

[a] Relative basicities and acidities refer to the reactions:

$$SHX + H_3S^+ \rightarrow SH_2X^+ + H_2S$$

$$SHX + HS^- \rightarrow SX^- + H_2S$$

[b] 4-31 + G data for anionic oxygen compounds from this research, other oxygen data from ref. 1.

Table 4. Geometrical and electron population data on CH_3OH, CH_3O^- and CH_3SH, CH_3S^-[a]

	CH_3OH	CH_3O^-	CH_3SH	CH_3S^-
$p(\sigma)$	0.35	0.33	0.53	0.42
$p(\pi)$	−0.03	0.28	−0.03	0.06
r(C—Y)	1.430	1.361	1.822	1.839
r(C—H) av.	1.081	1.122	1.079	1.092
$\Delta E(X, H)$ (kJ mol^{-1})	−64.0	−131.4	−125.6	−97.6

[a] $p(\sigma)$ and $p(\pi)$ are σ and π bond orders for the C—O and C—S bonds and obtained, as were the geometrical data, from calculations at 4-31G//4-31G level calculations (supplemented for sulfur molecules).

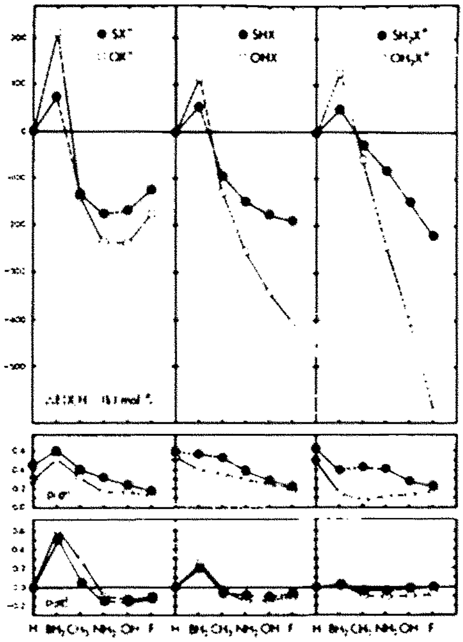

Fig. 2. Interaction energies (kJ mol^{-1}) and σ and π bond orders for SHX and SH$_3$X$^+$ series molecules from 6-31G##//4-31G(#) level calculations and SX$^-$ series molecules at 6-31+G##//4-31G(#) level. Included for comparison are results for the corresponding first row compounds (open circles; 4-31G//4-31G level calculations, 4-31+G//4-31G for the OX$^-$ series).

Interaction energies in the three sulfur series run parallel with those calculated for the oxygen analogues. Apart from the three S–BH$_2$ interactions, which like those for the analogous O–BH$_2$ cases are all stabilizing, the sulfur–substituent interaction energies are all negative. The trends across the NH$_2$, OH, F sequence show far less severe effects for sulfur than for oxygen, particularly for the cationic SH$_2$X$^+$ series compounds. ΔE(X, H) values for the BH$_2$ and CH$_3$ substituted molecules are very similar in the two groups, although SBH$_2^-$ cannot match the strong π-stabilization exhibited by OBH$_2^-$.

The relative energy data can be rationalized by assuming that σ-interactions dominate in all cases except those involving the π-acceptor BH$_2$ where the stronger π-bonding possible with the 1st row centre accounts for the much larger stabilization energy of OBH$_2^-$. The progressively more unfavourable interactions with the σ-acceptor substituents NH$_2$, OH, and F suggest that SH be classified as a weak σ-acceptor and SH$_2^+$ as a strong σ-acceptor. As may be expected on this view, the destabilization produced by these substituents is rather the more severe for the oxygen-containing molecules.

Further substitution of the methyl group has the same effect on molecular energy as it did at first, the interaction energy value of -191.6 kJ mol^{-1} being just short of twice the substituent interaction energies of SH·CH$_3$. With SF$_2$, however, the attachment of the second fluorine is 55 kJ mol^{-1} less destabilizing than the first, showing that the S—F bonds interact with each other, but much less strongly than do the P—F bonds in PF$_3$.[2e]

Acidities and basicities of SHX *compounds.* Basicity and acidity data follow the trends which might have been predicted. The substituted sulfur SHX compounds become progressively more acidic and less basic across the NH$_2$, OH, F sequence but the changes are much smaller than those calculated for the oxygen analogues.

The effects of methyl substitution on the acidity of methanol and methane thiol have been discussed already.[9] As DeFrees *et al.* point out, there are two separate hyperconjugative interactions between CH$_3$ and O$^-$ (or S$^-$), a destabilizing four-electron term (repulsion between filled orbitals on both centres) and a stabilizing two-electron term (resulting from overlap between the filled pπ orbitals on the anionic centre and the antibonding π-type C—H orbitals and producing a charge shift towards the CH$_3$ group). However, the effects in the CH$_3$O$^-$/CH$_3$OH systems contrast sharply with those in CH$_3$S$^-$/CH$_3$SH. At the much longer bond distances found in the 2nd row molecules hyperconjugation is very weak. C—H bond lengthening between CH$_3$SH and CH$_3$S$^-$ is only 1.3 pm compared with a 4.1 pm C—H bond length difference between CH$_3$O$^-$ and CH$_3$OH. Consequently, the shortening of the C—O bond in the anion (a very large 6.9 pm) produced by hyperconjugation becomes a 1.7 pm C—S bond lengthening in CH$_3$S$^-$!

The contrast between first and second row compounds is probably to be accounted for by the comparative absence of π-bonding in CH$_3$S$^-$. Note the very large change in π-bond order in CH$_3$OH/CH$_3$O$^-$ against an almost constant σ-bond order and the opposite situation in the second row compound. As a result, the methyl substituent is acid weakening in H$_2$S. Although *d* functions are not needed in the explanation for this behaviour, because the contribution made is similar in both CH$_3$SH and CH$_3$S$^-$, that contribution is not insignificant. Geometry optimization using basis sets without *d* functions uniformly leads to a C—S bond length some 9.0 pm longer than experiment whereas the discrepancy with supplemented basis set calculations is only about 1.0 pm; as noted elsewhere,[10] *d* functions appear to act in a marginal valence role in molecules of normal valency as well as in hypervalent compounds.[11]

CONCLUSIONS

Relative energy data on the sulfur-containing series SHX, SX$^-$ and SH$_2$X$^+$ follow very similar trends to those reported for the oxygen analogues and are readily accommodated by perturbation molecular orbital theory on the hypotheses:

(a) σ-interactions are predominant for the strong σ-acceptors NH$_2$, OH, F and account for substituent interaction energies which rise as charge is withdrawn from the anions SX$^-$, fall for SHX, and fall steeply for the cations SHX$^+$.[2] As in the corresponding oxygen series, all interactions are unfavourable, but the greater polarizability of the electron distribution in the second row case leads to a better toleration of the charge developed on the central atom and to much less severe destabilization.

(b) π-interactions are important with the π-acceptor substituent BH$_2$ but much less so than for the 1st row molecules. Hyperconjugation between CH$_3$ and S is much less in evidence than in the CH$_3$OH/CH$_3$O$^-$ case.

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