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The Electronic Structure of Siloxyl Sulfide, OSiS

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Recently the molecule OSiS has been prepared in an argon matrix by the reaction of SiS with atomic oxygen [1]. It was concluded on the basis of IR spectral studies that a silicon–sulfur double bond is present in this molecule. A true double bond has so far been found [2] only in SiS; force constant = 4.94 $\times 10^{-2}$ N/m^{-1}, which is only stable as a monomeric species at high temperature.

Semi-empirical molecular orbital calculations and energy localized molecular orbitals are presented below in an attempt to elucidate the nature of the electronic structure of siloxyl sulfide.

Calculations

The symmetry of the molecule ($C_{\infty v}$) requires that the molecule lie on the *z*-axis with the *y*-axis passing through the silicon atom. The silicon–oxygen bond distance [3] was set equal to 1.509 Å. The Si–S bond distance was allowed to vary from 1.70 Å to 3.25 Å. The only distance at which the system converged using the CNDO/2 method [4, 5] was 3.00 Å.

Similar calculations performed in the carbonyl sulfide molecule did not show the same type of behavior but rather converged to a minimum energy structure at the experimental geometry (d_{C-O} = 1.61 Å and d_{C-S} = 1.560 Å). Since it was felt that a S–Si distance of 3.00 Å was too long to be identified with a 'normal' S–Si bond distance (the sum of the Van der Waals radii are about 2.6–2.9 Å) [6], the molecular orbital calculations were repeated using the MNDO method [7] of Dewar *et al.* The structure of minimum energy was found to be a linear molecule with oxygen silicon distance of 1.54 Å and a silicon sulfur distance of 1.92 Å.The calculated standard heat of formation was 0.80 kcal mol^{-1}, very close to zero. The localized** molecular orbital (LMO) calculations were started from the MNDO canonical molecular orbitals and carried out by a previously published method [8–13].

TABLE I. Molecular Orbital Results for Siloxyl Sulfide.

a) *CNDO/2*

d_{Si-O} = 1.509 Å (assumed)
d_{Si-S} = 3.000 Å (calculated)
OSiS = 180°
E_{Total} = −32.32 au (-8.48×10^4 kJ/mole)
B·E = 0.43 au (1.13×10^3 kJ/mole)

Atomic Charges:
S = −0.116; Si = 0.407; O = −0.292

Orbital Charges:

S		Si	O	
3s	1.9872	1.7058	*2s*	1.7273
$3p_x$	1.9900	0.4734	$2p_x$	1.4957
$3p_y$	1.9900	0.4734	$2p_y$	1.4957
$3p_z$	0.1418	0.8397	$2p_z$	1.5732
$3d_{z^2}$	0.0066	0.0183		
$3d_{xz}$	0.0001	0.0408		
$3d_{yz}$	0.0001	0.0408		
$3d_{x^2-y^2}$	0.0000	0.0000		
$3d_{xy}$	0.0000	0.0000		

b) *MNDO*

d_{Si-O} = 1.541 Å (calculated)
d_{Si-S} = 1.916 Å (calculated)
ΔH_f° = 0.800 kcal mol^{-1}

Atomic Charges:
S = −0.326; Si = +0.861; O = −0.535

Results and Discussion

The molecular orbital calculation results are shown in Table I. As expected, both the oxygen and the sulfur atoms are negatively charged, while the silicon carries a small positive charge. The *d* orbitals of the silicon atom play a negligible role in the development of the electronic structure. In many binary sulfur–nitrides it has been observed that the *d*-orbitals of sulfur do not make any major contribution to the bonding. The sulfur *d*-orbital charges in this molecule are more than ten-fold lower than those observed in many binary sulfur–nitrogen ring systems and thus the *d*-type orbitals of both sulfur and silicon can be ignored in the analysis of the molecular electronic structure. This is probably due to their diffuse nature. The localized orbitals together with their percentage localizations* are presented in Table II. The molecule has eight occupied molecular orbitals which include two *sigma* bonds (Si–O and

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**The percentage localization is obtained by truncating the localized orbital so as to include only those atomic orbitals which are associated with atom(s) which participate in the formation of a chemical bond or lone pair electron and calculating $\sum_i (C_i^{LMO})^2 \times 100$.

TABLE II. Localized Molecular Orbitals for Siloxyl Sulfide.

LMO Type	Atomic Orbital Coefficients		% Localizations
Si–O σ bond	Si $3s$ +0.3531 $3p_z$ −0.4804	O $2s$ +0.2537 $2p_z$ −0.7238	94.37
Si–S σ bond	Si $3s$ +0.6730 $3p_z$ +0.2244	S $3p_z$ +0.5116 $3p_z$ +0.4847	99.99
S-lone pair	S $3s$ +0.8490 $3p_z$ −0.2017		76.14
O-lone pair	O $2s$ +0.9394 $2p_z$ +0.3293		99.08
Si–S π bonds	Si $3p_x$ +0.2977	S $3p_x$ +0.9293	95.22
Si–O π bonds	Si $3p_x$ +0.3706	O $2p_x$ +0.9058	95.78

Si–S); two lone pair orbitals, one on sulfur and one on oxygen; and four *pi* bonding orbitals, two localized between the silicon atom and the oxygen atom and two localized between the silicon atom and the sulfur atom.

The electronic structure can be viewed as:

$$|S\equiv Si\equiv O|$$

All the orbitals are more than 94% localized except for the lone pair orbital on the sulfur center. The lone pair orbital for the sulfur atom is not entirely localized (76.14%) on the sulfur atom but contains appreciable amounts of silicon $3s$ and $3p_z$ atomic orbitals. The most interesting feature of the electronic structure in this molecule is the extent of multiple bonding along the S–Si–O chain. The Si–O and Si–S bonds both have a high π character. Both of these bonds should exhibit a shorter than normal bond distance. The localized orbitals indicate that bond orders in excess of two are to be expected, even when the role of 'd' type orbitals of silicon are excluded from the analysis. It is not surprising that Schnockel finds evidence for a silicon–sulfur multiple bond [1]. The extent of mixing of the silicon $3p_x$ atomic orbital with either the $2p_x$ of the oxygen atom or the $3p_x$ of the sulfur atom is about the same leading one to suspect that the Si–O bond and the Si–S bonds are about the same in strength. This is not reflected in the corresponding force constants 9.0×10^{-2} and 4.9×10^{-2} N/m^{-1}, respectively. The difference is a reflection of the lower overlap integral between the silicon–sulfur orbitals as compared with the overlap between the silicon–oxygen orbitals.

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