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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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To cite this Article Müller, Robert and Heinze, Jürgen(1998) 'Stabilization of Oxidized Sulfur and Selenium Centers in Organic Chalcogens by Three-Electron Sulfur-Sulfur, Selenium-Selenium, and Sulfur-Selenium Bonds. A Theoretical Study Using the Semiempirical PM3 Method', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 557 — 560

To link to this Article: DOI: 10.1080/10426509808545995

URL: <http://dx.doi.org/10.1080/10426509808545995>

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STABILIZATION OF OXIDIZED SULFUR AND SELENIUM
CENTERS IN ORGANIC CHALCOGENS BY THREE-ELECTRON
SULFUR-SULFUR, SELENIUM-SELENIUM, AND
SULFUR-SELENIUM BONDS. A THEORETICAL STUDY USING
THE SEMIEMPIRICAL PM3 METHOD.

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Semiempirical computations at the Parimetric Method 3 (PM3) level confirmed an *intramolecular* stabilization of the radical cations of 1, ω -bis(methylchalcogeno)alkanes by 2-center 3-electron bonds. The formation of bi- and trimolecular associations was also investigated.

Keywords: three-electron bonds; organosulfur compounds;
organoselenium compounds; radical cations

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INTRODUCTION

Two-center, three-electron (2c-3e) bonds were first described in 1931 by Linus Pauling^[1]. Two of the electrons form a σ bond while the third is promoted into an antibonding σ^* level. Although 2c-3e sulfur-sulfur bonds were known for more than 20 years^[2], relative few informations were published for similar selenium-selenium and sulfur-selenium interactions. In order to quantify this kind of stabilization of sulfur and selenium radical cations, PM3-UHF calculations were realized for a series of open chain 1, ω -bis(methylchalcogeno)alkanes 1-3 (Figure 1) whose radical cations are known to form *intramolecular* 2c-3e bonds^[3].

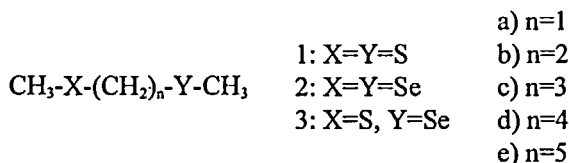


FIGURE 1: Studied 1, ω -bis(methylchalcogeno)alkanes

METHOD

All calculations have been made with the HyperChem package (release 5.01 for Windows 95, Hypercube Inc.) using the semiempirical Parimetric Method 3 (PM3) with Unrestricted Hartree-Fock field and Polak-Ribiere algorithm. Preliminary calculations performed for (H₂S)₂⁺⁺ and HS-(CH₂)_n-SH⁺⁺ (n=1 to 4) showed that the PM3 computations are less exact than *ab initio* results [4,5] but give nevertheless good *qualitative* informations of the general trends in 2c-3e bond formation.

RESULTS

PM3 computations revealed that the cyclic radical cations of 1, ω -bis(methylthio)alkanes **1** are stabilized by about 31.1 to 44.0 kcal mole⁻¹ towards their linear analogs. The same trend was also observed for the organoselenium radical cations **2** whose cyclic forms are even 65.6 to 83.0 kcal mole⁻¹ more stable. In the case of the mixed sulfur-selenium radical cations **3** the stabilization energy of the cyclic form was intermediate (46.2 to 64.2 kcal mole⁻¹) and could be predicted within 4% from the corresponding sulfur-sulfur and selenium-selenium 2c-3e interactions according to Clark [6]. Computing the gap energy ($E_{\text{HOMO}}-E_{\text{LUMO}}$) of the radical cations of **1-3** confirmed experimental results [3] indicating that the most favorable orbital overlap (characterized by the highest σ/σ^* separation - and thus the lowest λ_{max} in optical absorption spectra) was observed for the compounds with $n=3$.

Further computations showed that all radical cations of **1-3**, either linear or cyclic, can undergo dimerization into a dimeric radical cation with the corresponding neutral chalcogen. Dimerization reactions into a dimeric dication were however only observed for the organoselenium compounds **2**. Investigations of trimolecular complexes revealed that an association of a radical cation and two neutral molecules, or two radical cations and one neutral molecule, is generally stabilized towards the cyclic radical cations. Complexes formed by three radical cations are however unstable compared to three separate radical cations with intramolecular 2c-3e bonds, the only exception being **2a**.

These follow-up reactions, which are of various magnitude for all investigated radical cations, are likely the reason why the experimental measured oxidation peak potentials [3] can not be linearly correlated with the energy of the HOMO, computed at the PM3 level.

TABLE I: Results of PM3 computations. Dissociation energy of the cyclic radical cation (M_{X-Y}), gap energy (ΔE_{gap}), maximum absorption wavelength (λ_{max} / nm) [3], dissociation energy of bimolecular linear (BL) and cyclic (BC), and trimolecular complexes (T) with total charges +1, +2 and +3. Dissociation energies are given in kcal mole⁻¹ and the gap energy in eV. (a) same value as for the linear conformation; (b) not converged.

	1					2					3				
	a	b	c	d	e	a	b	c	d	e	a	b	c	d	e
M_{X-Y}	(a)	+31.1	+43.7	+44.0	+43.6	(a)	+65.6	+83.0	+78.9	+81.6	(a)	+46.2	+62.6	+63.3	+64.2
ΔE_{gap}	8.13	8.34	8.31	8.19	8.14	8.28	8.10	8.22	8.12	8.00	8.12	8.23	8.49	8.24	8.22
λ_{max}	660	525	440	460	475	680	550	440	460	470	620	550	435	435	470
BL_{+1}	+32.5	+14.3	+11.4	+10.8	+7.1	+113	+104	+20.0	+9.7	+9.5	+89.5	+67.3	+16.7	+7.1	+4.1
BC_{+1}	(a)	9.8	15.8	9.5	14.5	(a)	100	111	89.0	102	(a)	66.2	50.2	47.7	45.6
BL_{+2}	-33.8	-71.3	-59.9	-49.0	-41.6	+11.8	+19.3	-47.6	-46.6	-46.3	-2.7	-12.6	-56.4	-47.8	-46.5
BC_{+2}	(a)	(b)	(b)	-52.4	-47.7	(a)	+27.2	+16.3	+5.6	+31.0	(a)	-21.8	-23.9	-24.8	-24.2
T_{+1}	+49.2	+28.1	+22.2	+15.1	+22.8	+218	+217	+239	+182	+223	+168	+128	+103	+87.2	+97.0
T_{+2}	-90.6	(b)	(b)	(b)	(b)	+167	+193	+147	+126	+175	+103	+76.4	+55.3	+46.8	+37.2
T_{+3}	-119	(b)	(b)	(b)	(b)	+12.9	-13.7	-9.0	-13.2	-18.0	-43.7	-79.7	-84.7	-84.7	-83.3

Acknowledgments

Financial support is gratefully acknowledged from the Deutsche Forschungsgemeinschaft (Postdoctoral Fellowship R.M.) and the Fonds der Chemischen Industrie.

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