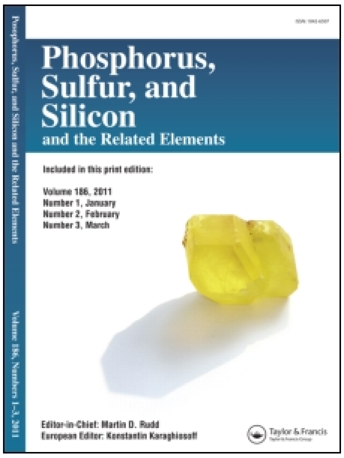

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Chemistry of Mixed Sulfur-, Selenium-, or Tellurium- and Silicon-, or Tin-Containing Heterocycles

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Lone pair ionization energies for 1,5-dichalcogenocanes containing endocyclic 3,7-R_2Si groups and the parent 1,5-dichalcogenocanes, estimated from the TCNE charge-transfer wavelength maxima, are in good agreement with ionization energies directly obtained from photoelectron spectroscopy. These data indicate the occurrence of substantial intra-annular interaction between the chalcogen atoms and silyl groups, consistent with the well-known β-effect of silicon and the novel β-disilyl effect, when R (in R_2Si) is Me_3Si.

Keywords 1,5-dithiocane; 5-thiaselenocane; β-disilyl effect; β-stannyl effect; β-silyl effect; chalcogen heterocycles; photoelectron spectroscopy; TCNE charge transfer bands

INTRODUCTION

Eight-membered rings play an important role in chalcogen chemistry. Elemental sulfur ordinarily exists in the solid state as the crown-shaped cyclooctasulfur, S_8; cyclooctaselenium, Se_8, and cyclooctatellurium, Te_8, are also known. Sequential one-electron oxidation of these "*cyclo*-[-E_8-]" ring systems affords "*cyclo*-[-E_8-]$^{+2}$" dications

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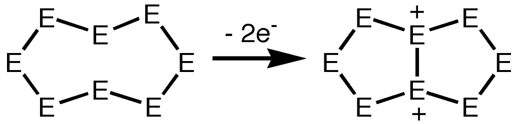
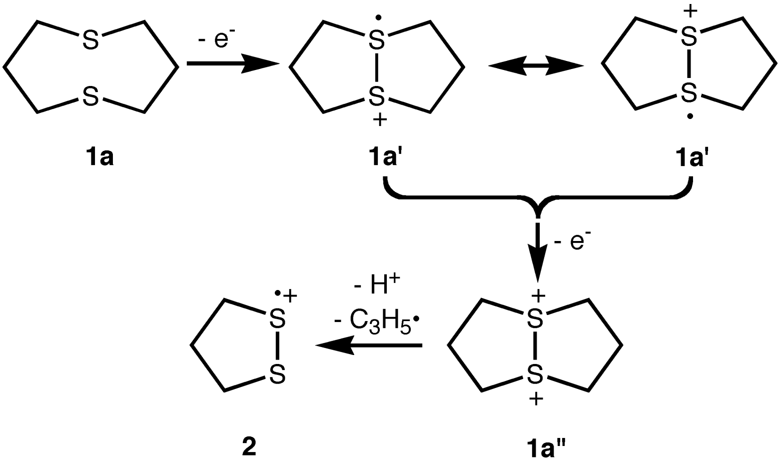


SCHEME 1 Two-electron oxidation of cyclooctachalcogens E_8 to dications E_8^{+2}.

(E = S, Se or Te) with transannular chalcogen-chalcogen bonding,[1] a reaction also seen with eight-membered ring "*cyclo*-[-E(CH_2)$_3$-]$_2$" heterocycles 1,5-dithiocane (**1a**), 1,5-diselenocane (**1c**) and 1,5-ditellurocane (**1d**) (Schemes 1 and 2).[2–5] These reactions, involving lone-pair facilitated oxidation and transannular through-space interactions, are relevant to the investigation of redox and metal coordination chemistry and electron transfer in biological systems and materials. For example, both the radical cation and dication of **1a** are unusually stable, the oxidation potential of **1a** is extremely low as compared to that of ordinary sulfides, and the oxidation is electrochemically reversible, in contrast to the case with ordinary sulfides.[6,7] The base peak of the mass spectrum of **1a** is the 1,2-dithiolane radical cation **2**, resulting from fragmentation of the radical cation or dication of **1a**.[8] Neighboring lone-pair effects have also been proposed for photo-oxidation of **1a**, involving the intermediacy of the corresponding persulfoxide.[9]

In the present work, two new types of chalcogen-containing eight-membered rings have been synthesized: 1) those having two different chalcogen atoms, e.g. 5-thiaselenocane (**1b**), a compound of type



SCHEME 2 Oxidation products of **1a**.

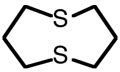
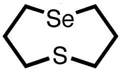
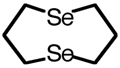
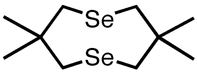
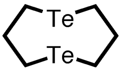
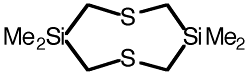
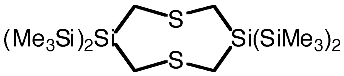
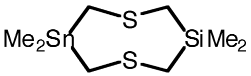
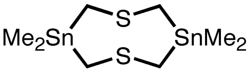
"*cyclo*-[-E$(CH_2)_3$E$'$$(CH_2)_3$-]" in which one- and two-electron oxidation induces intramolecular interactions of different chalcogens E and E$'$; 2) those having β-situated silicon groups, e.g. 3,3,7,7-tetramethyl- or 3,3,7,7-tetrakis-(trimethylsilyl)-3,7-disila-1,5-dithiocane (**3a** and **3b**, respectively, in Table I; also **3c–g**), or β-R_2Sn groups, compounds of type "*cyclo*-[-E$CH_2MR_2CH_2$-$]_2$," in which β-effects of silicon, tin, or silicon-silicon orbitals on one-electron oxidation at proximate chalcogen centers can be studied. We sought to compare and contrast the behavior of these latter two types of systems on one-electron oxidation with the behavior of the previously studied "*cyclo*-[-E_8-]" and "*cyclo*-[-E$(CH_2)_3$-$]_2$" heterocycles.[10–13]

While transannular interactions in such ring systems can be explored in detail using the techniques of photoelectron spectroscopy (PES) in conjunction with theoretical calculations, a simpler probe of these interactions involves determination of the long wavelength maximum of the tetracyanoethylene charge-transfer (TCNE CT) band in the ultraviolet spectrum.[14] We find that this data, presented below, correlates very well in the majority of cases studied with the lowest ionization energies determined by PES.[13]

RESULTS AND DISCUSSION

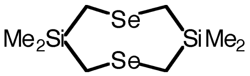
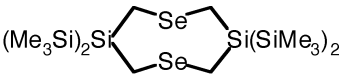
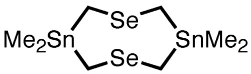
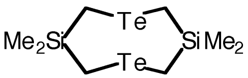
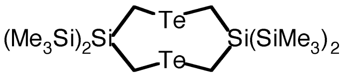
It has previously been reported that ionization energies may be obtained spectroscopically by measurement of the CT transition of TCNE complexes of alkyl and aryl derivatives of sulfur, selenium and tellurium.[14] Consequently, the $\lambda_{\max}$ of the TCNE CT complexes of the compounds synthesized in this study were determined and are reported in Table I. The compounds were dissolved in CH_2Cl_2, distilled from P_2O_5 under nitrogen, and mixed with multiply recrystallized TCNE in 1:1 molar ratios at concentrations in the range 1–9 mM. In cases where the ionization energy of the compound is too low, e.g., with most tellurium compounds, stable absorption spectra were not observed, presumably owing to electron transfer followed by fast decomposition. A simple expression, shown in Equation 1, relates the ionization energy of the donor, I_D, to the frequency of the CT band, ν_{CT}; m and c are constants. The method was validated by comparing the ionization energy determined from the CT transition and the lowest ionization energy measured by PES. The ionization energies of the compounds for which PES have been measured are also given in Table I. A plot of PES ionization energy versus CT band maxima for these and other compounds prepared in this project gave, with one exception, an excellent linear correlation between the ionization energies directly measured by PES and those calculated from the charge transfer transition, thereby validating

TABLE I Comparative TCNE-CT and PES Data for Selected 8-Membered Ring Heterocycles

Entry	Heterocycle	TCNE-CT, nm (ε)[a] [UV $\lambda_{\max}$]	PES IP_1, IP_2[ΔIP], eV
1	 **1a**	520 (125)	8.27, 8.69 [0.42]
2	 **1b**	564	8.11, 8.57 [0.46]
3	 **1c**	584 (73)	8.00, 8.35 [0.35]
4	 **1d**	598	—
5	 **1e**	—[b]	7.59, 7.91 [0.32]
6	 **3a**	584 (181)	7.90, 8.10 [0.20]
7	 **3b**	628 (85)	7.51, 7.72 [0.22]
8	 **3c**	622 (423)	7.66, 7.88 [0.22]
9	 **3d**	—[b]	7.50, 7.74 [0.24]

(Continued on next page)

TABLE I Comparative TCNE-CT and PES Data for Selected 8-Membered Ring Heterocycles *(Continued)*

Entry	Heterocycle	TCNE-CT, nm (ε)[a] [UV λ_{max}]	PES IP_1, $IP_2[\Delta IP]$, eV
10	 **3e**	638 (97)	7.71, 7.94 [0.23]
11	 **3f**	656 (44)	—
12	 **3g**	—[b]	7.42, 7.60 [0.18]
13	 **3h**	—[b]	7.38, 7.62 [0.24]
14	 **3i**	—[b]	7.04, 7.21 [0.17]

[a]Solvent is CH_2Cl_2; [b]reacts with TCNE.

the method for this class of compounds.[13]

$$h\nu_{\mathrm{CT}} = mI_D + c \tag{1}$$

From the data in Table I we conclude that neighboring C–Si, C–Sn, and Si–Si groups in these conformationally constrained heterocycles reduce the lowest ionization energies of chalcogen compounds and that β-Si–Si groups are particularly effective in this regard. For compounds **1a**, **1c**, and **1e**, the two peaks observed by PES correspond to the antisymmetric (HOMO) and symmetric (HOMO-1) 3*p*-, 4*p*- and 5*p*-lone pair orbitals, respectively. The corresponding ionization energies show the expected decrease in the order S > Se > Te.[15] The lone pair splitting similarly decrease in the order S (0.42 eV) > Se (0.35 eV) > Te (0.32 eV) indicating that the lone pair orbital overlap also decreases in the order S > Se > Te. The molecular basis for the large ΔIP in 5-thiaselenocane

(**1b**) will be discussed separately.[16] Substitution of the 3,6-CH_2 moieties in the 1,5-dichalcogenocanes by Me_2Si or Me_2Sn groups result in a significant lowering of the ionization energies, compared to the small effect of a Me_2C group (**1d**), e.g. **1a** > **1d** > **3a** > **3d**. This is reasonable because there is a better energy match of C–Sn than C–Si than C–C orbitals with sulfur $3p$ lone pair orbitals, which should destabilize the HOMO in the order C–Sn > C–Si > C–C. This destabilization is reflected in the ionization energies of **3d** (7.50 eV) compared to that for **3a** (7.90 eV) and **1a** (8.27 eV). Similar, but somewhat smaller effects are seen when comparing selenium compounds **3e**, **3g** and **1c** and tellurium compounds **3h** and **1e**. The effects are smaller in these latter cases because the lower ionization energy of the Se $4p$ and Te $5p$ orbitals leads to poorer energy matches with the C–Sn and C–Si orbitals compared to the S $3p$ orbitals. The substantial lowering of ionization energies for **3b**, **3f,** and **3i**, each of which contains four β-Si–Si bonds, is due to significant interactions between the chalcogen p-orbitals and the Si–Si orbitals, which from X-ray crystallographic studies, are well positioned for optimum orbital interaction. The lone pair-lone pair splitting in these cases depend not only on through-space interactions (as in the cases of **1a**, **1c,** and **1d**) but through-bond interactions as well, as discussed elsewhere for **3b**.[10]

The interactions of the Group 16 and 18 elements in heterocycles such as **3a–i** may make the chalcogen atoms more effective n-donors in complexation with metals. We describe elsewhere investigation of the stoichiometric one- and two-electron oxidation of several of the above heterocycles together with parallel studies involving cyclic voltammetry, along with efforts to isolate and characterize the oxidation products.[16]

REFERENCES

[1] T. S. Cameron, R. J. Deeth, I. Dionne, H. Du, H. D. B. Jenkins, I. Krossing, J. Passmore, and H. Roobottom, *Inorg. Chem.*, **39,** 5614–5631 (2000).

[2] W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98,** 3055–3056 (1976).

[3] W. K. Musker, *Acc. Chem. Res.*, **13,** 200–206 (1980).

[4] N. Furukawa, *Bull. Chem. Soc. Jpn.*, **70,** 2571–2591 (1997).

[5] H. Fujihara, T. Ninoi, R. Akaishi, T. Erata, and N. Furukawa, *Tetrahedron Lett.*, **32,** 4537–4540 (1991).

[6] G. S. Wilson, D .D. Swanson, J. T. Klug, R. S. Glass, M. D. Ryan, and W. K. Musker, *J. Am. Chem. Soc.,* **101,** 1040–1042 (1979).

[7] M. D. Ryan, D. D. Swanson, R. S. Glass, and G. S. Wilson, *J. Phys. Chem.,* **85,** 1069–1075 (1981).

[8] W. K. Musker, B. V. Gorewit, P. B. Roush, and T. L. Wolford, *J. Org. Chem.,* **43,** 3235–3236 (1978).

[9] E. L. Clennan and S. E. Hightower, *J. Org. Chem.,* **71,** 1247–1250 (2006).

[10] R. S. Glass, E. Block, E. Lorance, U. I. Zakai, J. Jin, and S.-Z. Zhang, *J. Am. Chem. Soc.*, **128,** 12,685–12,692 (2006).

[11] E. Block, E. V. Dikarev, R. S. Glass, J. Jin, B. Li, X. Li, and S.-Z. Zhang, *J. Am. Chem. Soc.*, **128,** 14,949–14,961 (2006).

[12] E. Block, R. S. Glass, E. V. Dikarev, N. E. Gruhn, J. Jin, B. Li, E. Lorance, U. I. Zakai, and S.-Z. Zhang, *Heteroatom Chem.*, **18,** 509–515 (2007).

[13] R. S. Glass, E. Block, N. E. Gruhn, J. Jin, E. Lorance, U. I. Zakai, and S.-Z. Zhang, *J. Org. Chem.*, **72,** 8290–8297 (2007).

[14] J. E. Frey, T. Aiello, D. N. Beaman, H. Hutson, S. R. Lang, and J. J. Puckett, *J. Org. Chem.*, **60,** 2891–2901 (1995).

[15] M. R. Detty and M. E. Logan, *Adv. Phys. Org. Chem.*, **39,** 79–142 (2004).

[16] D. H. Evans, N. A. Macias-Ruvalcaba, N. E. Gruhn, E. Lorance, N. Okumura, U. I. Zakai, J. Jin, S.-Z. Zhang, E. V. Dikarev, B. Li, E. Block, and R. S. Glass. manuscript in preparation.