M Ű E G Y E T E M 1 7 8 2

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MOLECULAR AND ELECTRONIC STRUCTURE OF UNSATURATED SELENIUM AND TELLURIUM COMPOUNDS

Ph. D. thesis

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Introduction

Theoretical chemistry is a traditional research field at the Budapest University of Technology and Economics Department of Inorganic and Analytical Chemistry. The main research topic is the investigation of reaction mechanism, stabilization of short-lived molecules, calculation of geometry, electronic structure and spectroscopic properties of molecules. These properties were studied by both theoretical chemistry methods and our self-made HeI ultraviolet photoelectron spectrometer (UPS).

My research work was performed in co-operation with the research group of University of Rennes (Ecole Nationale Supérieure de Chemie de Rennes, France). The research group under the direction of Dr. Jean-Claude Guillemin deals with synthesizing new molecules bearing interesting and usually unstable structures. The method of the collaboration is that the French group plans the synthesis of the new compounds and carries out preparative work, and we in turn study the molecules from the theoretical aspect and with photoelectron spectroscopy.

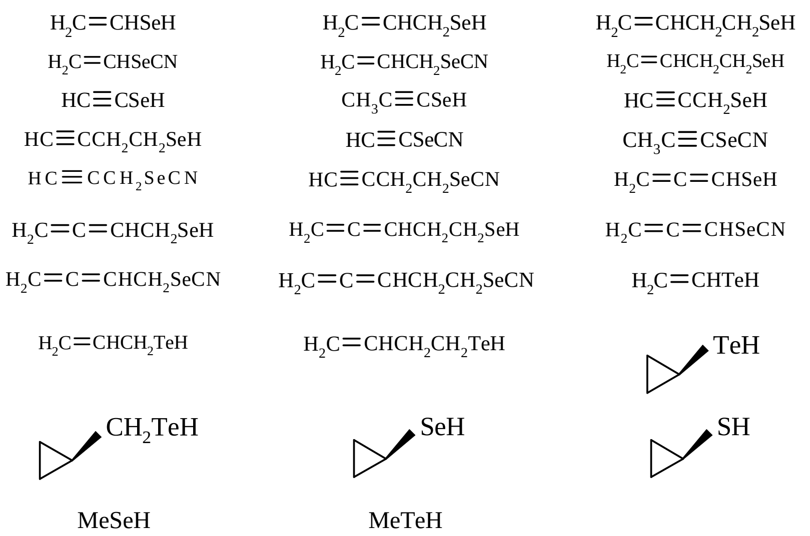
Since the studied molecules (mainly selenols and tellurols) are unstable, it was not possible to deliver them. Therefore I actively took part in the preparative work so I could transform certain synthesis for the photoelectron spectroscopy measurements that needs very pure materials in many cases.

In my thesis such selenols, selenocyanates and tellurols were investigated, in which the heteroatom containing group is situated next to an unsaturated group. The majority of the compounds are new, so the photoelectron spectroscopic measurements were a great tool for investigating their structures. My aim was to map the conjugation in molecules. Up until now, tellurols and unsaturated aliphatic selenols have not been studied by photoelectron spectroscopy in the literature.

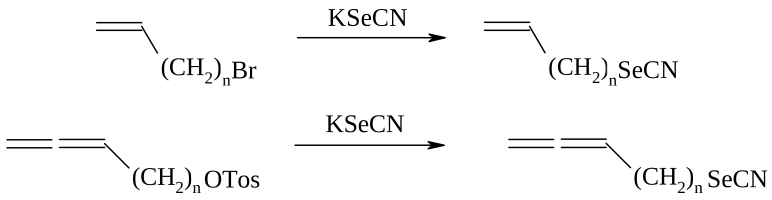
My thesis first considered selenium compounds containing alkenyl group, later selenium compounds containing allenyl and alkynyl groups and finally alkenetellurols and cyclopropanetellurols.

Preparative work

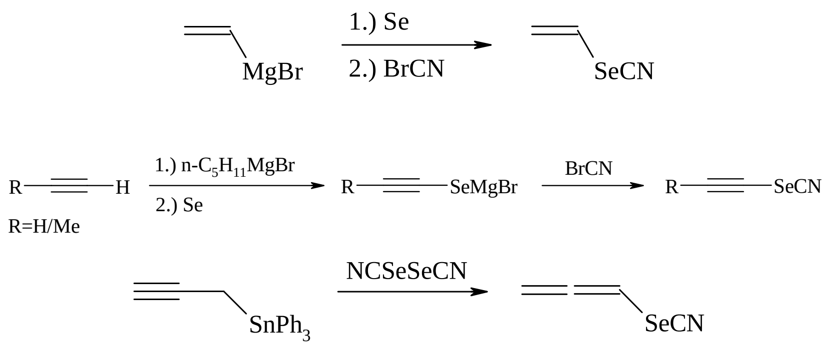
The following compounds were investigated in the thesis, from which I synthesized ten selenols one selenocyanate and six tellurols.



Alkenyl and alkadenyl selenocyanates were prepared according to the scheme below:



Those molecules where SeCN group is situated right next to the unsaturated group were synthesized using the following methods:



Selenols were prepared with $LiAlH_4$ or $AlHCl_2$ reagents from selenocyanates:

$$\text{R-SeCN} \xrightarrow[\text{2. Succinic acid}]{\text{1. LiAlH}_4\text{ / AlHCl}_2} \text{R-SeH}$$

Tellurols were prepared from ditellurides:

$$\text{R-Te-Te-R} \xrightarrow[\text{Ph}_2\text{Te}_2\text{ cat.}]{\text{nBu}_3\text{SnH}} \text{R-TeH}$$

Eleven novel compounds have been synthesized by the author.

Photoelectron spectroscopy

He I photoelectron spectra were recorded on an instrument made by the Department. The resolution was $\Delta E / E = 7 * 10^{-3}$ during the measurements. For internal calibration N_2 and methyl iodide were used. To interpret the PE spectra I compared the shape and position of the bands to those of related molecules whose PE bands have been assigned. Also I compared the recorded vertical ionization energies with the results of quantum chemical calculations.

Because of the instability of the investigated compounds, those were prepared just before the measurements by distilling them into a trap cooled with liquid nitrogen and designed for working in high vacuum. Before recording the spectra the trap was joined to the UPS apparatus, liquid nitrogen cooling was removed and the trap was warmed up to -110ºC. The by-products were removed by distillation. During the procedure, the temperature has been gradually increased. The spectrum was recorded at that temperature where the vapour pressure of the compound was high enough and contamination was not observed.

Computational methods

Quantum chemical calculations were performed for all the investigated molecules by the Gaussian 98 and Gaussian 03 program packages. All of the structures were optimized at the MP2/cc-pVTZ and the B3LYP/cc-pVTZ levels of theory. The stationary points were characterized by second-derivative calculations using the same model chemistry. The relative energies were corrected using the zero-point vibrational energies. The ionization energies were calculated at the ROVGF/cc-pVTZ level of theory on the optimized geometry. For comparison I also carried out single-point HF/cc-pVTZ calculations on the geometries obtained above.

New results

1. On the basis of the photoelectron spectra of alkenyl selenocyanates and selenols a strong direct conjugation was detected in etheneselenol and vinyl selenocyanate between the C=C double bond and the lone electron pair of selenium or the π system of the SeCN group, respectively. In allyl derivatives hyperconjugation was detected between the σ(C–Se) bond and the double bond. In but-3-enyl-1-derivatives only inductive effect was observed.
2. I synthesized five new compounds from alkadienyl selenols and selenocyanates. I found that in allenyl derivatives substituted in α position the effect of direct conjugation is stronger than the hyperconjugation. I pointed out that the result of the two interactions is a shorter Se–C bond in propadieneselenol than in etheneselenol. In β substituted allenyl derivatives weak but well observable

hyperconjugation interaction was detected. In γ substituted derivatives no significant interaction was detected.

3. I synthesized two new compounds from alkynyl derivatives. In ethynyl derivatives stronger direct conjugation was observed than in vinyl derivatives. In propargyl compounds hyperconjugation is the ruling effect. In but-3-inyl-1- derivatives only inductive effect was observed.
4. I synthesized three new tellurol compounds. On the basis of the photoelectron spectra in ethenetellurol strong conjugation was observed between the C=C double bond and the lone electron pair of tellurium atom. In prop-2-ene-1-tellurol the hyperconjugation interaction is the most important effect. In cyclopropanetellurol different interactions were clarified between the conformers. In cyclopropylmethanetellurol a stronger hyperconjugation interaction was detected than in prop-2-ene-1-tellurol.

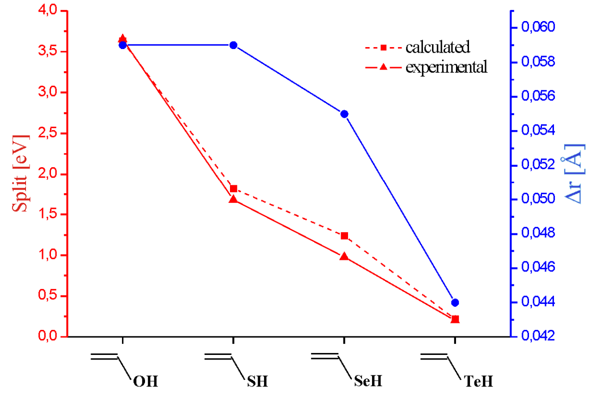


Figure 1.
Trend of the direct conjugation in vinyl calcogen hydrides. The split of the interacting orbitals and the alteration of the C-X (X=O, S, Se, Te) bond length.

5. On the basis of the photoelectron spectra and the calculated bond lengths, in vinyl calcogen hydrides a decreasing direct conjugation between the lone electron pair of X atom (X=O, S, Se, Te) and the double bond was found from oxygen to tellurium (Figure 1). However in allyl calcogen hydrides hyperconjugation is increasing from oxygen to tellurium (Figure 2). No direct interaction could be observed between the lone electron pair of X (X=S, Se, Te) and the three-membered ring in the cyclopropyl derivatives. Instead, an interaction between the σ(C–Te) and e_2 orbitals has been shown. This hyperconjugation-like effect increases from S to Te (Figure 3). Also, an increasing hyperconjugation could be observed from S to Te in cyclopropylmethyl derivatives (Figure 4).

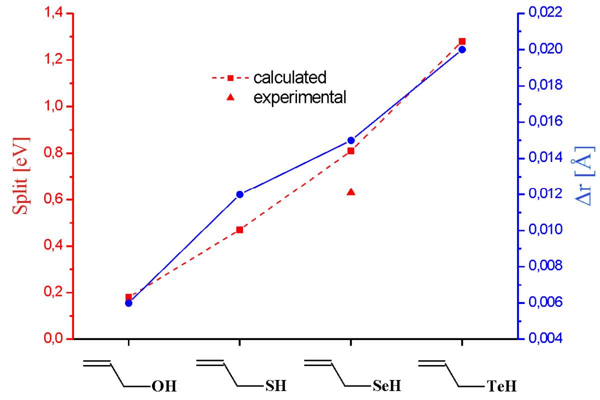


Figure 2.
Trend of the hyperconjugation in allyl calcogen hydrides. The split of the interacting orbitals and the alteration of the C-X (X=O, S, Se, Te) bond length.

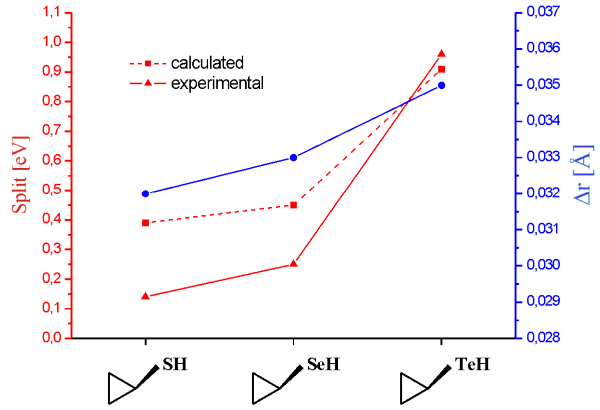


Figure 3.
Trend of the conjugation in cyclopropyl calcogen hydrides. The split of the interacting orbitals and the alteration of the C-X (X=O, S, Se, Te) bond length.

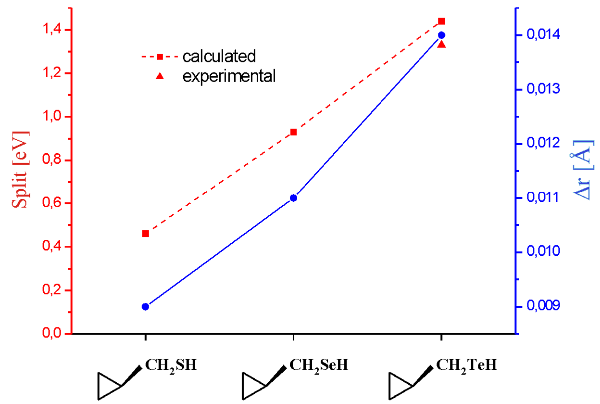


Figure 4.
Trend of the hyperconjugation in cyclopropylmethyl calcogen hydrides. The split of the interacting orbitals and the alteration of the C-X (X=S, Se, Te) bond length.

Publications

1. Gábor Bajor, Tamás Veszprémi, El Hassan Riague, Jean-Claude Guillemin *Alkenyl Selenols and Selenocyanates: Synthesis, Spectroscopic Characterization by Photoelectron Spectroscopy and Quantum Chemical Study* Chemistry – A European Journal **2004**, *10*, 3649-3656. (Impact Factor: 5.015)

2. Jean-Claude Guillemin, El Hassan Riague, Gábor Bajor, Brahim Khater, Tamás Veszprémi *Allenyl and Alkynyl Selenols and Selenocyanates. Synthesis, Spectroscopic Characterization and Quantum Chemical Study* Organometallics **2007**, *26*, 2507-2518. (Impact Factor: 3.632)

3. Brahim Khater, Jean-Claude Guillemin, Gábor Bajor, Tamás Veszprémi *Functionalized Tellurols: Synthesis, Spectroscopic Characterization by Photoelectron Spectroscopy, and Quantum Chemical Study* Inorganic Chemistry **2008**, *47*, 1502-1511. (Impact Factor: 3.911)

Publications not included in the thesis:

4. Farman Ullah, Gábor Bajor, Tamás Veszprémi, Peter G. Jones, Joachim Heinicke *Stabilization of Unsymmetrically Annelated Imidazol-2-ylidenes with Respect to Their Higher Group 14 Homologues by n-/π-HOMO Inversion* Angewandte Chemie International Edition **2007**, *46*, 2697-2700. (Impact Factor: 10.232)

5. Farman Ullah, Olaf Kühl, Gábor Bajor, Tamás Veszprémi, Peter G. Jones, Joachim Heinicke *Transition Metal Complexes of N-Heterocyclic Germylenes* (elküldve a *Chem. Eur. J.* folyóirathoz)

6. Farman Ullah, Anca I. Oprea, Markus K. Kindermann, Gábor Bajor, Tamás Veszprémi, Joachim Heinicke *Pyrido [a]-anellated 1,2,3-Diazasiloles and 1,2,3-Diazagermol-2-ylidenes* (elküldve a *J. Organomet. Chem.* folyóirathoz)