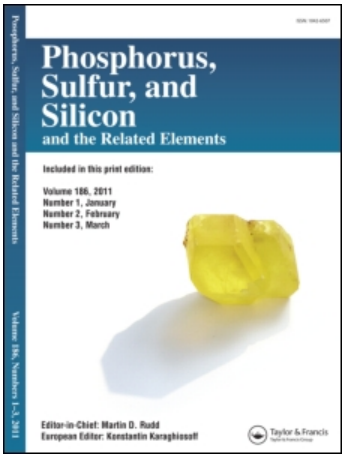


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# Quantum Mechanical Studies of Organometallic Materials Containing the Se-Te Bond

Antonio Grassi; Kurt J. Irgolic; Giuseppe M. Lombardo; Giuseppe C. Pappalardo

**To cite this Article** Grassi, Antonio , Irgolic, Kurt J. , Lombardo, Giuseppe M. and Pappalardo, Giuseppe C.(1998) 'Quantum Mechanical Studies of Organometallic Materials Containing the Se-Te Bond', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 417 — 422
**To link to this Article: DOI:** 10.1080/10426509808545968
**URL:** http://dx.doi.org/10.1080/10426509808545968

*Phosphorus Sulphur and Silicon*
Vols. 136, 137 & 138 pp. 417–422
Reprints available directly from the publisher
Photocopying permitted by license only



# QUANTUM MECHANICAL STUDIES OF ORGANOMETALLIC MATERIALS CONTAINING THE Se-Te BOND

ANTONIO GRASSI[a], KURT J. IRGOLIC[b], GIUSEPPE M. LOMBARDO[a], and GIUSEPPE C. PAPPALARDO[a]
[a]Dipartimento di Scienze Chimiche, Cattedra di Chimica Generale, Facolta di Farmacia, Universita di Catania, Viale A. Doria 6, I-95125 Catania, Italy; [b]Institute for Analytical Chemistry, Karl-Franzens-Universität Graz, Universitätsplatz 1, A-8010 Graz, Austria



This study was carried out to establish the reliability of ab-initio (Huzinaga, 3-21G*, STO-3G* basis sets) and pseudo-potential (LANDL2DZ basis set) quantum mechanical methods for molecules containing the Te-Se-Te group. Bond lengths and bond energies were calculated for the diatomic model compounds Se-Se, Se-Te, and Te-Te and for the molecule bis(phenyltelluro) selenide, $(C_6H_5Te)_2Se$. The theoretical results for the diatomic models were compared with the experimental data. The conclusions were: i) the pseudo-potential method is not suited to deal with systems containg Se and Te atoms; ii) the ab-initio method works acceptably with the Huzinaga and the 3-21G* basis sets; iii) the inclusion of electron correlation (MP2) increases the quality of the results; iv) a final choice between the Huzinaga and the 3-21G* basis sets can be made on the basis of new experimental data for molecules with the Se-Te group.

Keywords: Te-Se-Te group, bis(phenyltelluro)selenide, ab-initio calculations, pseudo-potential calculations, electron correlation

# 418 QUANTUM MECHANICAL STUDIES OF ORGANOMETALLIC MATERIALS CONTAINING THE Se-Te BOND

## INTRODUCTION

The production of thin films of metal chalcogenides by metal organic chemical vapor deposition (MOCVD) is of growing importance in material science [1,2]. Organometallic compounds with a Te-Se-Te group have great potential as precursors for the production of new semiconducting materials, but have not yet been investigated in detail. Isolated nanometric particles with size-controlled band structures seem to be obtainable from organometallic compounds containing short chains of chalcogens in all combinations. Theoretical and experimental information about the electronic structure of molecules with two or more different chalcogen atoms bonded to each other is still lacking, although such compounds, for instance, bis(phenyltelluro) selenide, are available[3].



This paper reports the results of ab-initio and pseudo-potential calculations including correlation energy at the MP2 level with the goal to characterize the Se-Te bond and to obtain information about the stability of the Te-Se-Te group in bis(phenyltelluro) selenide[4]. To test the accuracy of the basis sets available for compounds containing Se and Te, the diatomic molecules Se-Se, Se-Te, and Te-Te, for which experimental dissociation energies and bond lengths are known, were studied[4].

## CALCULATIONAL METHODS

Calculations were performed with ab-initio (STO-3G*, 3-21G*, Huzinaga basis sets[5]) and pseudo-potential (LANL2DZ) methods of

the GAUSSIAN 94 package[6]. The total energies of the molecules were calculated with full optimizationof the geometries at the HF level. The energy values were refined by inclusion of the electronic correlation effects using the Møller-Plesset second-order perturbation theory (MP2)[7]. The bond strenght was evaluated as the difference between the total energy of the molecule and the sum of the energies of the non-bonded fragments. All calculations were performed in unrestricted Hartree-Fock (UHF).



## RESULTS AND DISCUSSION

The pseudo-potential approximation in calculating the bond energies for the diatomic Se-Se, Se-Te, and Te-Te failed (Table 1).

The calculated bond strenghts are negative at the HF level and approximately 50% lower than the experimental values at the MP2 level. The HF STO-3G* calculations provided bond strenghts of the same order of magnitude as the experimental values. For Se-Te the experimental and calculated bond strenghts agree quite well, whereas the calculated value for Se-Se is 12 kcal/mol higher and for Te-Te 7 kcal/mol lower than the experimental bond strength. These results indicate, that the error associated with the calculation of the atomic energy - particularly for heavy atoms - with the STO-3G* basis set may vary with atomic number.

The HF 3-21G* and the Huzinaga calculations produced values 50% lower than the experimental bond strenghths. Inclusion of the electronic correlation at the MP2 level of the theory in all the basis sets raised the bond energies. With the Huzinaga and 3-21G* basis sets the calculated

energies agree acceptably with the experimental data. Inclusion of the correlation effects in the STO-3G* and LANL2DZ methods increased the bond energies and led to significant disagreement with the experimental data by overstimation (STO-3G*) or understimation (LANL2DZ). In conclusion the Huzinaga and 3-21G* ab-initio methods including MP2 provide reliable bond energies for molecules containing Se and Te atoms; the inclusion of electron correlation is important.



The bond lengths calculated with ab-initio Huzinaga and 3-21G* methods agree well with the experimental data for Se-Se and Se-Te, whereas STO-3G* and LANL2DZ methods produce unacceptable results (Table 1). Therefore, the Huzinaga and 3-21G* basis sets appear to be suited for calculations on molecules containing Se and Te atoms.

The bond strengths for the Se-Te bond in bis(phenyltelluro) selenide obtained with the Huzinaga and the 3-21G* basis sets did not agree (Table 1). Because 3-21G* contains more base functions than the Huzinaga basis set, the 3-21G* value of 66 kcal/mol could be closer to the truth than the Huzinaga value (81 kcal/mol). However, the stabilization effects on the Se-Te bond in bis(phenyltelluro) selenide are expected to be quite different from the effect in the diatomic Se-Te. To arrive at a definitive decision, which basis set with or without correlation effects reproduces nature best, the UV and fluorescence spectral properties of bis(phenyltelluro) selenide are being studied to obtain information about the electronic structure of this molecule.

TABLE 1 Experimental and calculated bond dissociation energies (kcal/mol) and bond distances (Å)[a]

| group | Bond Energies | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | exp | Ab initio | | | | | | pseudo pot. | |
| | | Huzinaga | | 3-21G* | | STO-3G* | | LANL2DZ | |
| | | HF | MP2 | HF | MP2 | HF | MP2 | HF | MP2 |
| Se-Se | 79.49 | 28.95 | 71.35 | 41.46 | 83.38 | 91.97 | 122.25 | -1.77 | 36.78 |
| Se-Te | 69.69 | 25.56 | 65.12 | 35.34 | 74.30 | 69.45 | 97.80 | -1.07 | 34.26 |
| Te-Te | 62.09 | 22.99 | 59.20 | 29.29 | 65.24 | 55.24 | 78.87 | -1.84 | 30.26 |
| Se-Te[b] | | 9.52 | 81.87 | 21.59 | 66.22 | 32.49 | 86.64 | -2.91 | 30.09 |

| group | Bond Lengths | | | | |
|---|---|---|---|---|---|
| | exp | Huzinaga | 3-21G* | STO-3G* | LANL2DZ |
| Se-Se | 2.1660 | 2.1536 | 2.1404 | 2.0299 | 2.2680 |
| Se-Te | - | 2.3532 | 2.3414 | 2.2398 | 2.4371 |
| Te-Te | 2.5574 | 2.5579 | 2.5557 | 2.4636 | 2.6191 |
| Se-Te[b] | - | 2.548 | 2.528 | 2.414 | 2.639 |

[a] All calculations were performed in the UHF approximation. The bond lengths were calculated at the HF level.

[b] Se-Te in $(C_6H_5Te)_2Se$

**Acknowledgement**

These investigations were partially supported by MURST and CNR (Italy).

**References**

[1.] C. A. Estrada, R. A. Zingaro, E. A. Meyers, P. M. Nair and M. T. S. Nair, *Thin Solid Films,* **247**, 298 (1994), and references therein.

[2.] P. O'Brien and T. Trindade, *Chemistry of Materials,* **9,** 523 (1997).
[3.] S. Hauge and O. Vikane, *Acta Chim. Scand.,* **27,** 3596 (1973).
[4.] R. C. West and D. R. Lide (Eds.), *Handbook of Chemistry and Physics,* 75th ed. CRC Press, Boca Raton, FL, USA 1995.
[5] S. Huzinaga, *Gaussian basis sets for molecular calculations.* Elsevier, Amsterdam, 1994.
[6] GAUSSIAN 94, Gaussian Inc., Pittsburgh, PA, 1994-1995.
[7] C. Møller and M. S. Plesset, *Phys. Rev.* **46,** 618 (1934).