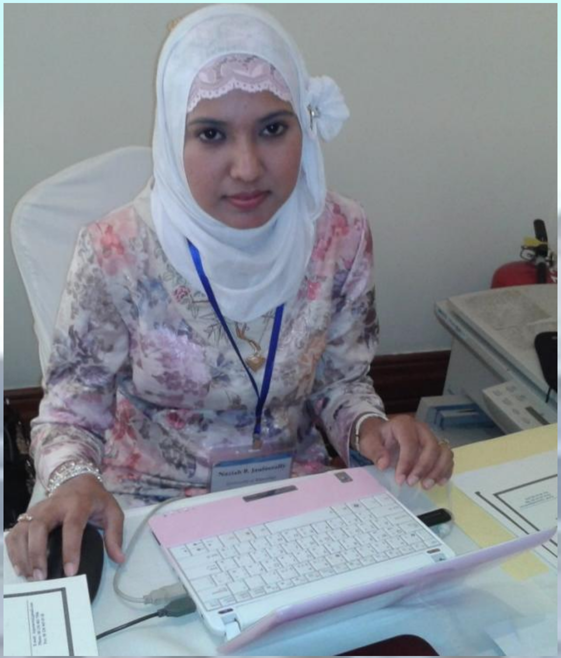
Structures, Energetics and Stabilities of Novel Telluro-ketones

By Mrs Naziah Jaufeerally

Myself

Mrs Naziah Jaufeerally



PhD scholar

Prof Ponnadurai Ramasami

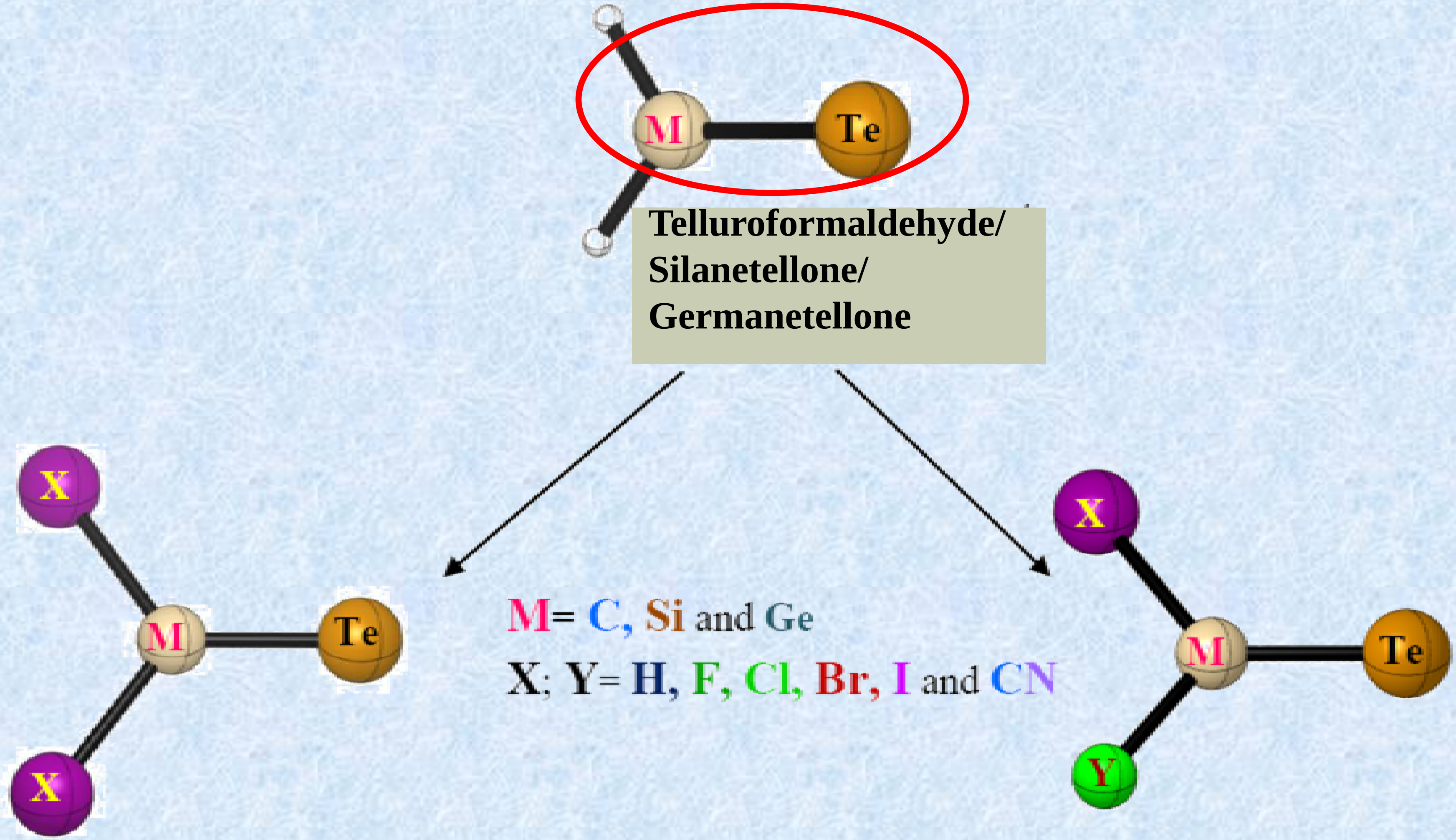
University of Mauritius

Faculty of Science | Department of Chemistry

$<\Psi|H|\Psi^*>=E<\Psi|\Psi^*>$

Computational Chemistry

Target Molecules

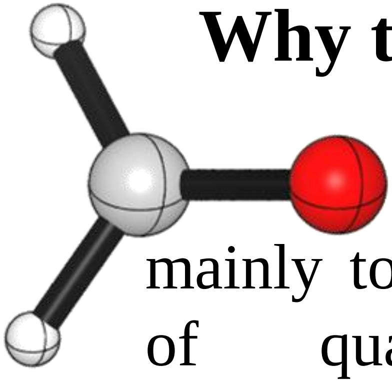


**Telluroformaldehyde/
Silanetellone/
Germanetellone**

M= C, Si and Ge

X; Y= H, F, Cl, Br, I and CN

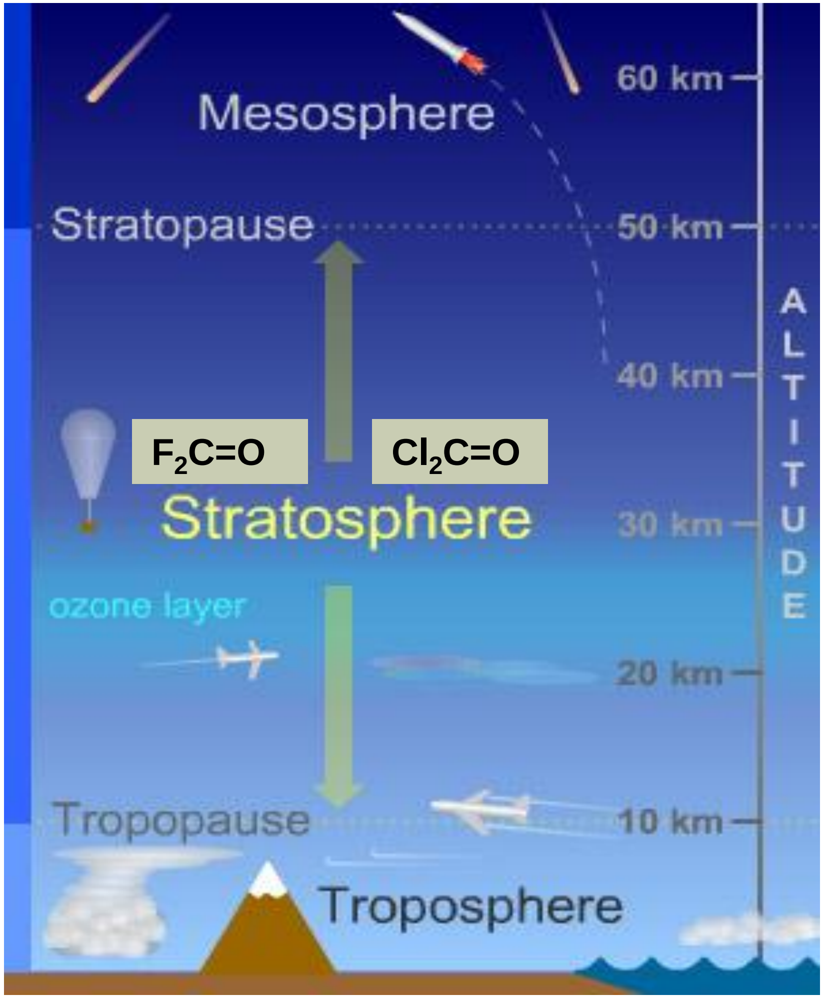
Why the study of Heavy Congeners of $H_2C=O$?



mainly to check the reliability of quantum mechanical computing methods

C=O group- important organic moiety in industry and biology

$X_2C=O$ (X=F and Cl) major products of photolysis of halomethanes in presence of oxygen



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Thio- and Seleno- analogues

– Important intermediates in sulfur and selenium containing molecules

– Composition of nucleic acid and ribose sugars of some active metabolites

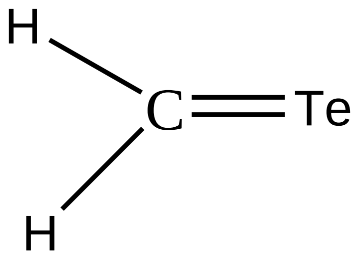
– Useful anti-tumour drugs

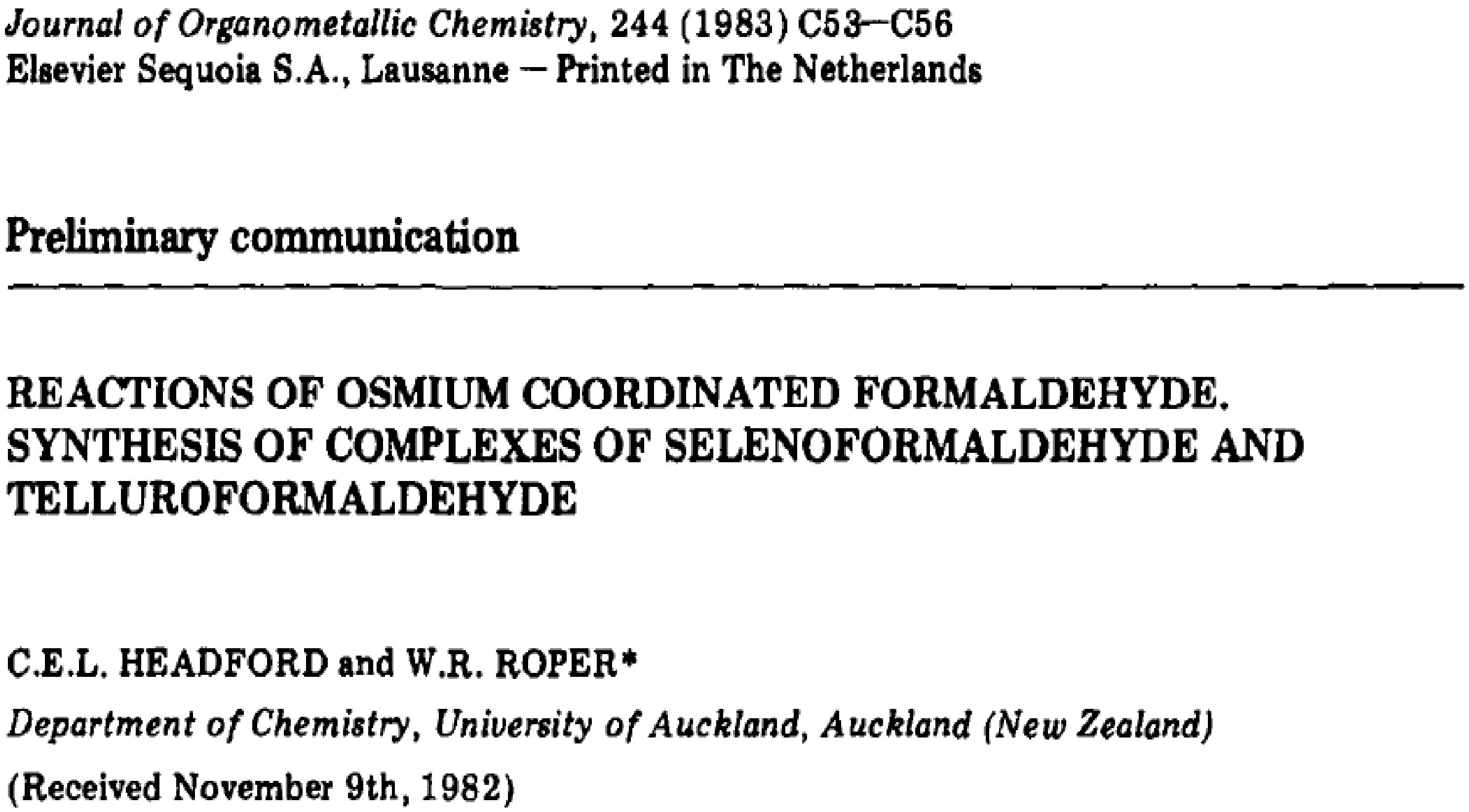
But the literature of telluro-ketones is scarce.

Despite

Telluroformaldehyde complexes were first synthesized in 1983.

Telluroformaldehyde




Journal of Organometallic Chemistry, 244 (1983) C53—C56
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

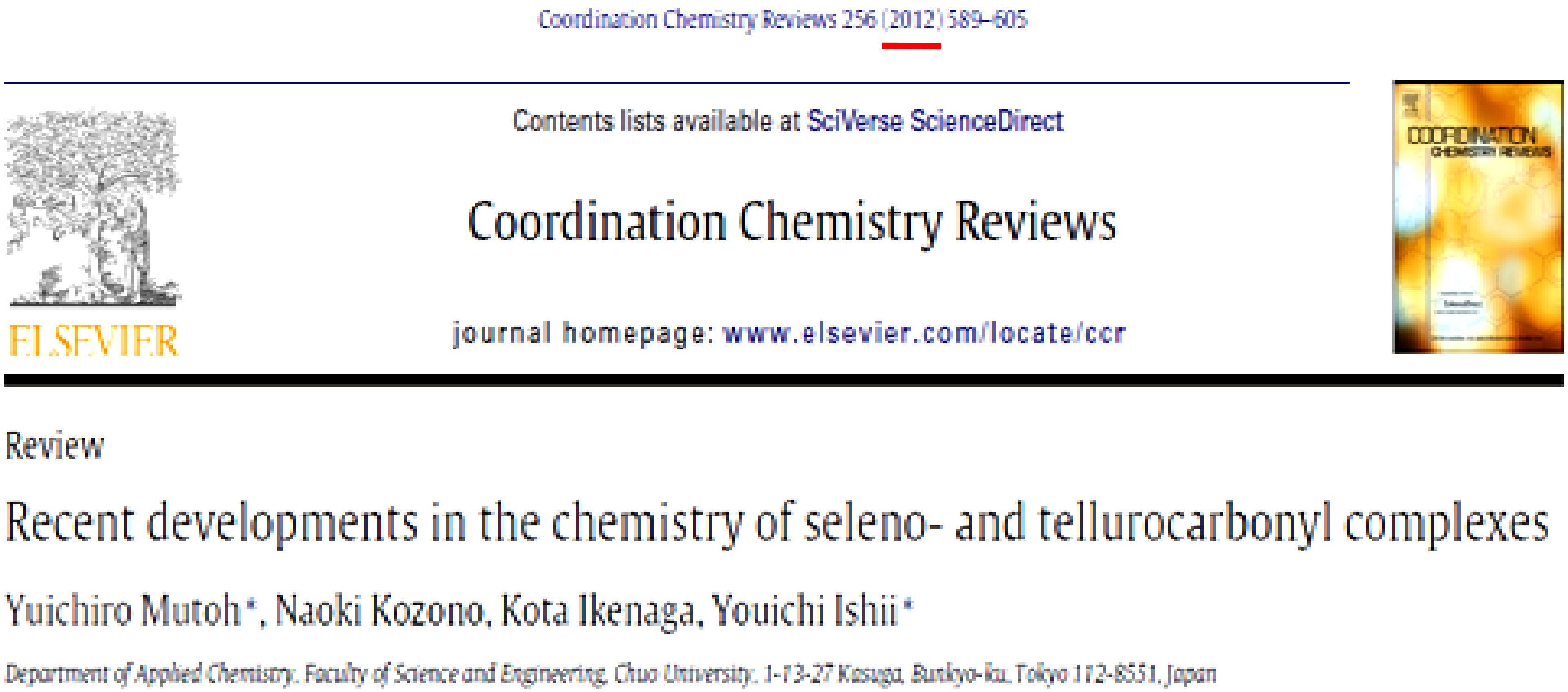
REACTIONS OF OSMIUM COORDINATED FORMALDEHYDE. SYNTHESIS OF COMPLEXES OF SELENOFORMALDEHYDE AND TELLUROFORMALDEHYDE

C.E.L. HEADFORD and W.R. ROPER*
Department of Chemistry, University of Auckland, Auckland (New Zealand)

(Received November 9th, 1982)

However, nowadays there is a quest for tellurium containing compounds or tellurocarbonyl compounds.

Importance of Telluro-ketones



Coordination Chemistry Reviews 256 (2012) 589–605

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journal homepage: www.elsevier.com/locate/ccr

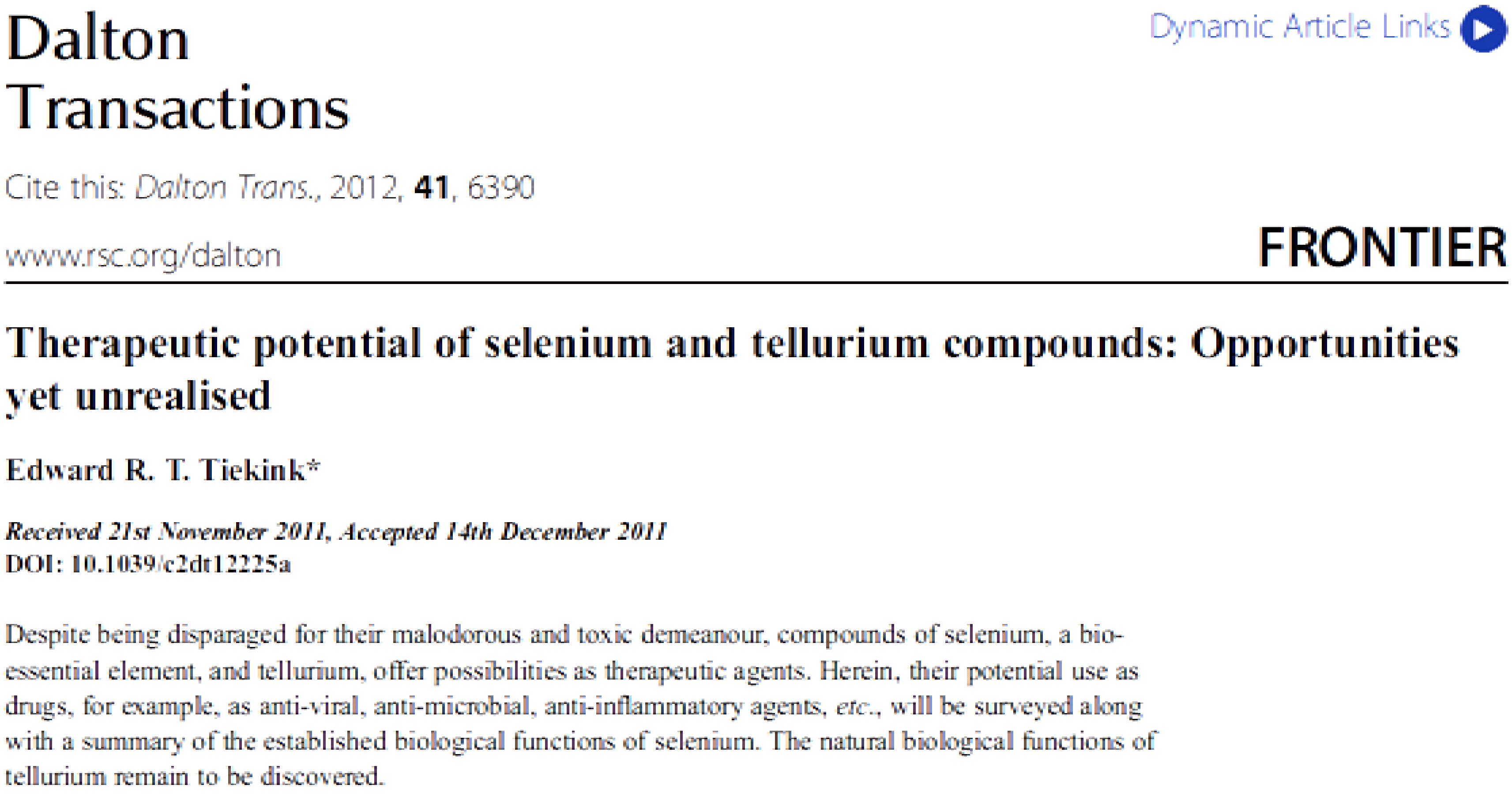
Review

Recent developments in the chemistry of seleno- and tellurocarbonyl complexes

Yuichiro Mutoh*, Naoki Kozono, Kota Ikenaga, Youichi Ishii*

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Importance of Telluro-ketones



Dalton
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Cite this: *Dalton Trans.*, 2012, **41**, 6390

www.rsc.org/dalton

FRONTIER

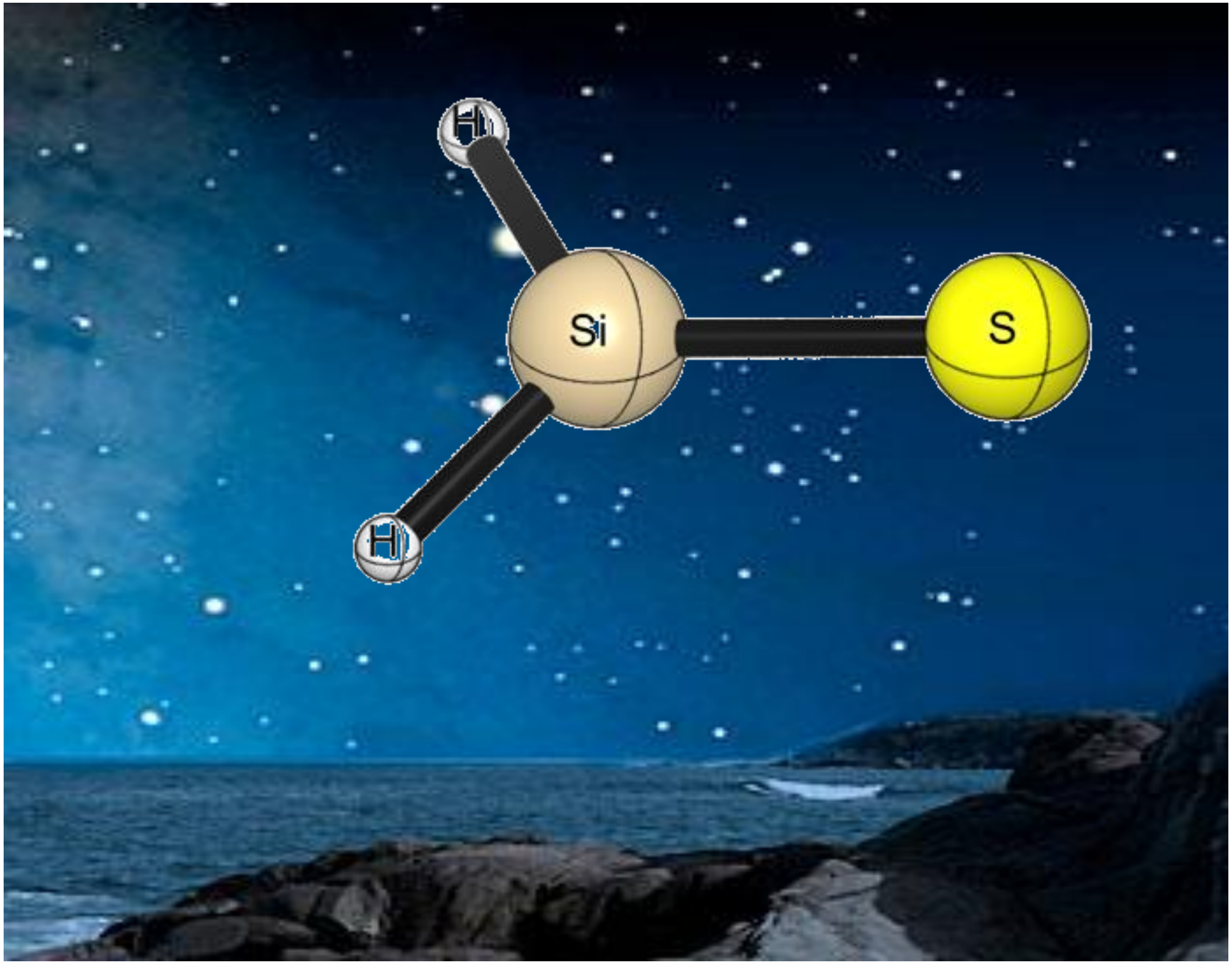
Therapeutic potential of selenium and tellurium compounds: Opportunities yet unrealised

Edward R. T. Tiekink*

Received 21st November 2011, Accepted 14th December 2011
DOI: 10.1039/c2dt12225a

Despite being disparaged for their malodorous and toxic demeanour, compounds of selenium, a bio-essential element, and tellurium, offer possibilities as therapeutic agents. Herein, their potential use as drugs, for example, as anti-viral, anti-microbial, anti-inflammatory agents, *etc.*, will be surveyed along with a summary of the established biological functions of selenium. The natural biological functions of tellurium remain to be discovered.

Monomeric $H_2Si{=}S$ has reached the STARS!



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Why Limited literature for Telluro-ketones?

Theoretical exploration has been scarce due to:

- Lack of well-tested basis sets for Te atom
- Limited computing resources

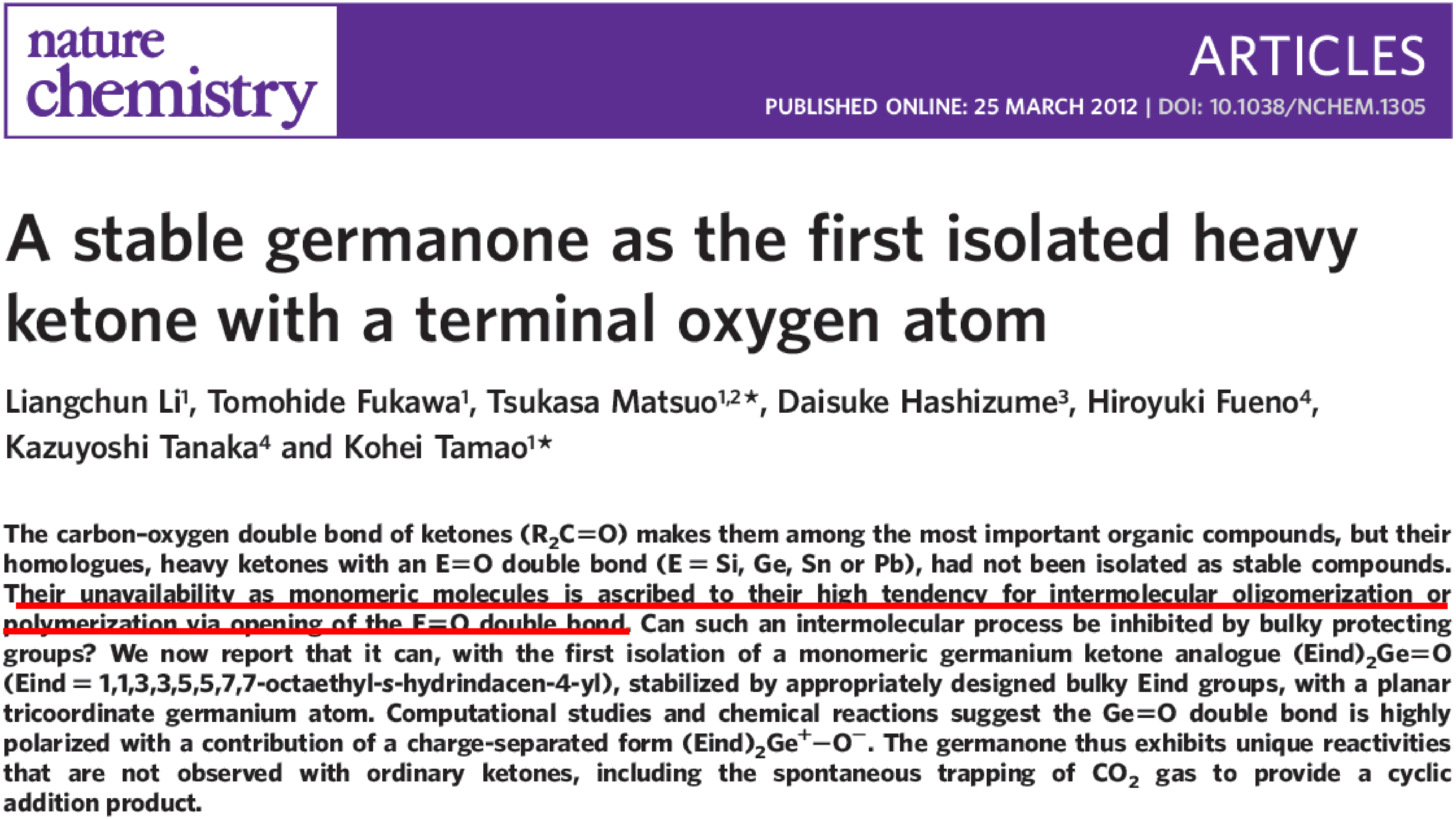
Why Limited literature for Telluro-ketones?

The lack of experimental studies is often ascribed to:

- The semipolar nature of the A=E bond (A=C, Si and Ge; E=O, S, Se and Te)

- High tendency for the A=E to open up and undergo intermolecular reactions

Stable Monomeric Germanone



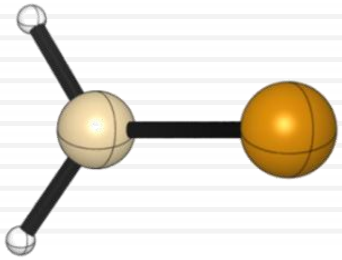
nature chemistry
ARTICLES

| DOI: 10.1038/NCHEM.1305

A stable germanone as the first isolated heavy ketone with a terminal oxygen atom

Liangchun Li[1], Tomohide Fukawa[1], Tsukasa Matsuo[1,2]*, Daisuke Hashizume[3], Hiroyuki Fueno[4], Kazuyoshi Tanaka[4] and Kohei Tamao[1]*

The carbon–oxygen double bond of ketones ($R_2C{=}O$) makes them among the most important organic compounds, but their homologues, heavy ketones with an E=O double bond (E = Si, Ge, Sn or Pb), had not been isolated as stable compounds. Their unavailability as monomeric molecules is ascribed to their high tendency for intermolecular oligomerization or polymerization via opening of the E=O double bond. Can such an intermolecular process be inhibited by bulky protecting groups? We now report that it can, with the first isolation of a monomeric germanium ketone analogue $(\mathrm{Eind})_2\mathrm{Ge{=}O}$ (Eind = 1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl), stabilized by appropriately designed bulky Eind groups, with a planar tricoordinate germanium atom. Computational studies and chemical reactions suggest the Ge=O double bond is highly polarized with a contribution of a charge-separated form $(\mathrm{Eind})_2\mathrm{Ge}^{+}{-}\mathrm{O}^{-}$. The germanone thus exhibits unique reactivities that are not observed with ordinary ketones, including the spontaneous trapping of CO_2 gas to provide a cyclic addition product.



Objectives of this research work

Telluro-ketones

Molecular geometries

Ionization Potentials

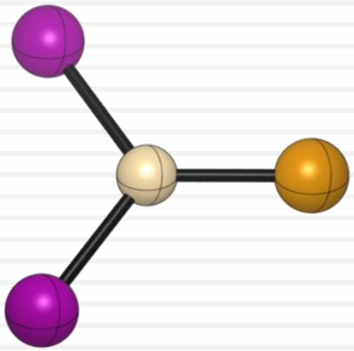
Electron Affinities

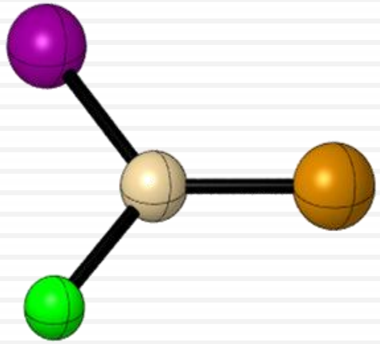
Singlet-Triplet Splittings

HOMO-LUMO gaps

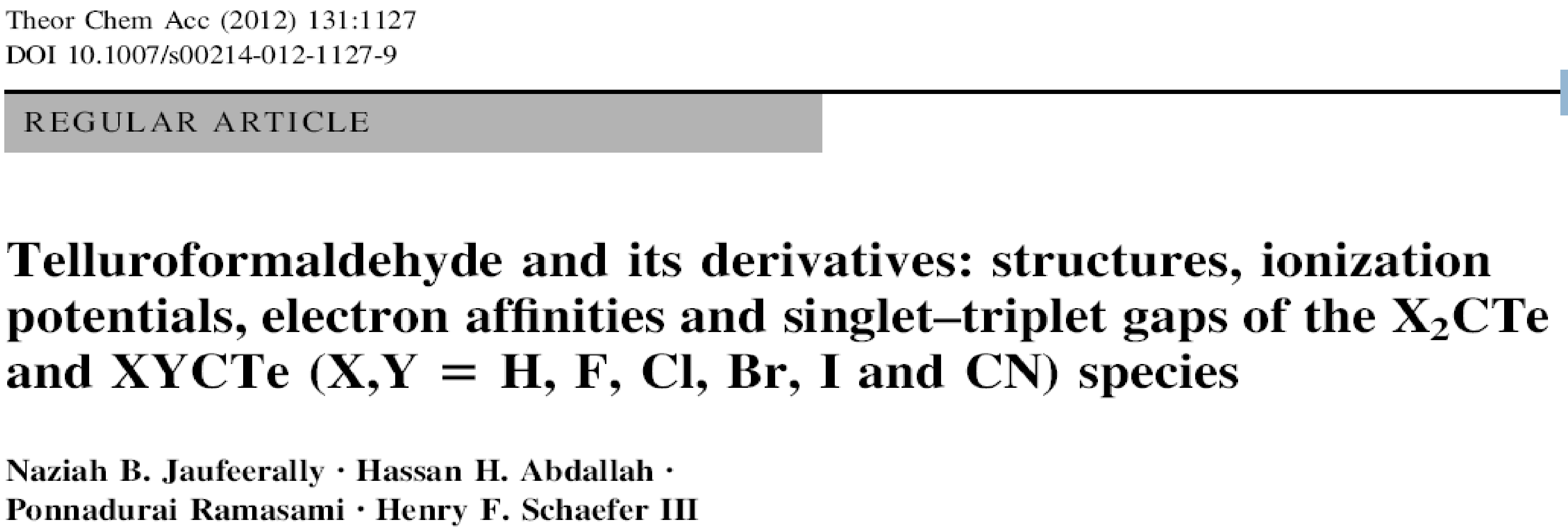
Kinetics

Isomeriz-ations





Our Findings

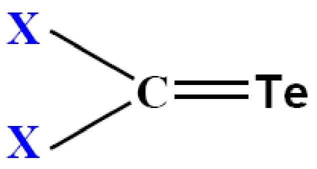


Theor Chem Acc (2012) 131:1127
DOI 10.1007/s00214-012-1127-9

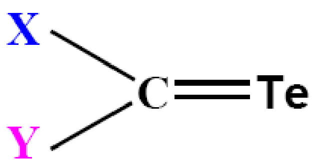
REGULAR ARTICLE

Telluroformaldehyde and its derivatives: structures, ionization potentials, electron affinities and singlet–triplet gaps of the X_2CTe and XYCTe (X,Y = H, F, Cl, Br, I and CN) species

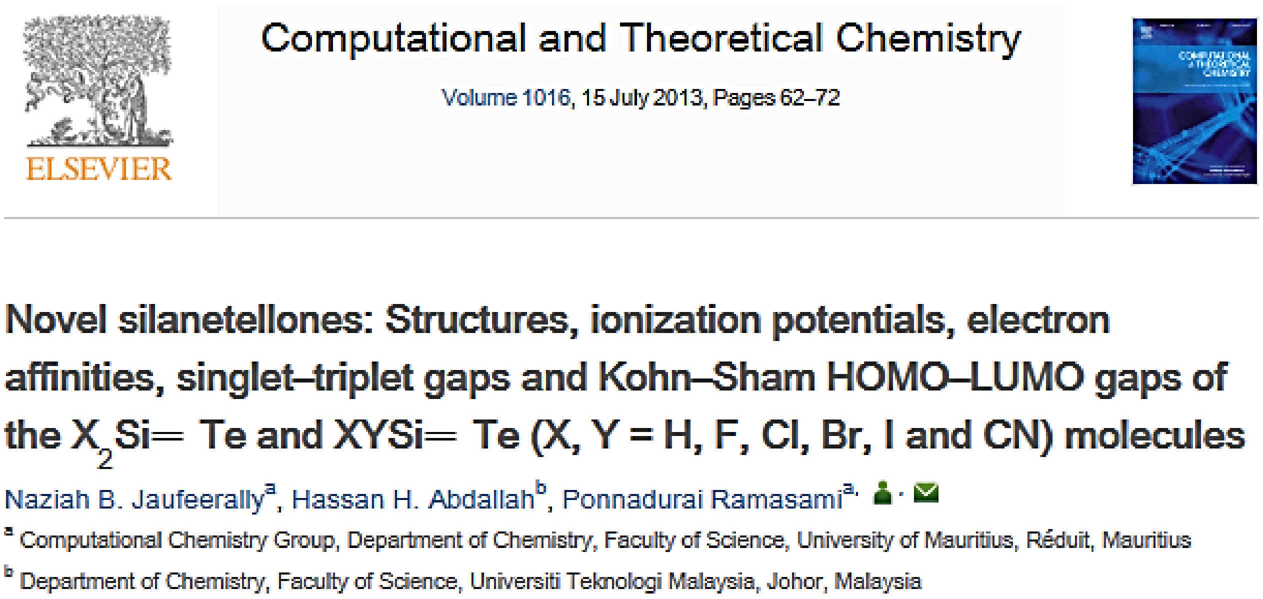
Naziah B. Jaufeerally · Hassan H. Abdallah ·
Ponnadurai Ramasami · Henry F. Schaefer III



X	H	F	Cl	Br	I	CN



X	H	H	H	H	H	F	F	F	F	Cl	Cl	Cl	Br	Br
Y	F	Cl	Br	I	CN	Cl	Br	I	CN	Br	I	CN	I	CN



Computational and Theoretical Chemistry

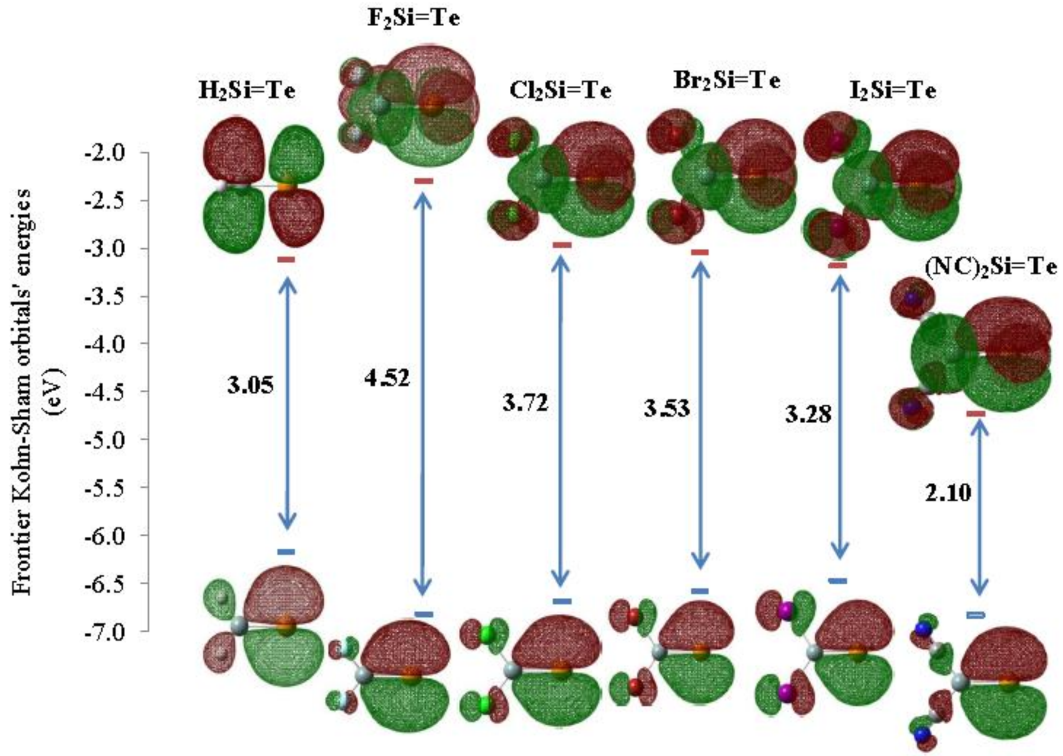
Volume 1016, 15 July 2013, Pages 62–72

Novel silanetellones: Structures, ionization potentials, electron affinities, singlet–triplet gaps and Kohn–Sham HOMO–LUMO gaps of the X_2Si= Te and XYSi= Te (X, Y = H, F, Cl, Br, I and CN) molecules

Naziah B. Jaufeerally[a], Hassan H. Abdallah[b], Ponnadurai Ramasami[a,]

[a] Computational Chemistry Group, Department of Chemistry, Faculty of Science, University of Mauritius, Réduit, Mauritius

[b] Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, Johor, Malaysia



Our Findings

The kinetic and thermodynamic stabilities of the telluro-ketones were always questioned by reviewers.

Back to literature…

How others have stabilized some of the known heavy ketones?

Has any stable telluro-ketone been synthesized and isolated so far?

Communication

First Stable Germanetellones: Syntheses and Crystal Structures of the Heaviest Germanium−Chalcogen Double-Bond Compound

Norihiro Tokitoh , Tsuyoshi Matsumoto , and Renji Okazaki *
Department of Chemistry Graduate School of Science The University of Tokyo 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

J. Am. Chem. Soc., 1997, *119* (9), pp 2337-2338
DOI: 10.1021/ja963517c
Publication Date (Web): March 5, 1997
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CAS Section: Organometallic and Organometalloidal Compounds

Your current credentials do not allow retrieval of the full text.

J. Am. Chem. Soc. **1999,** *121,* 8811−8824

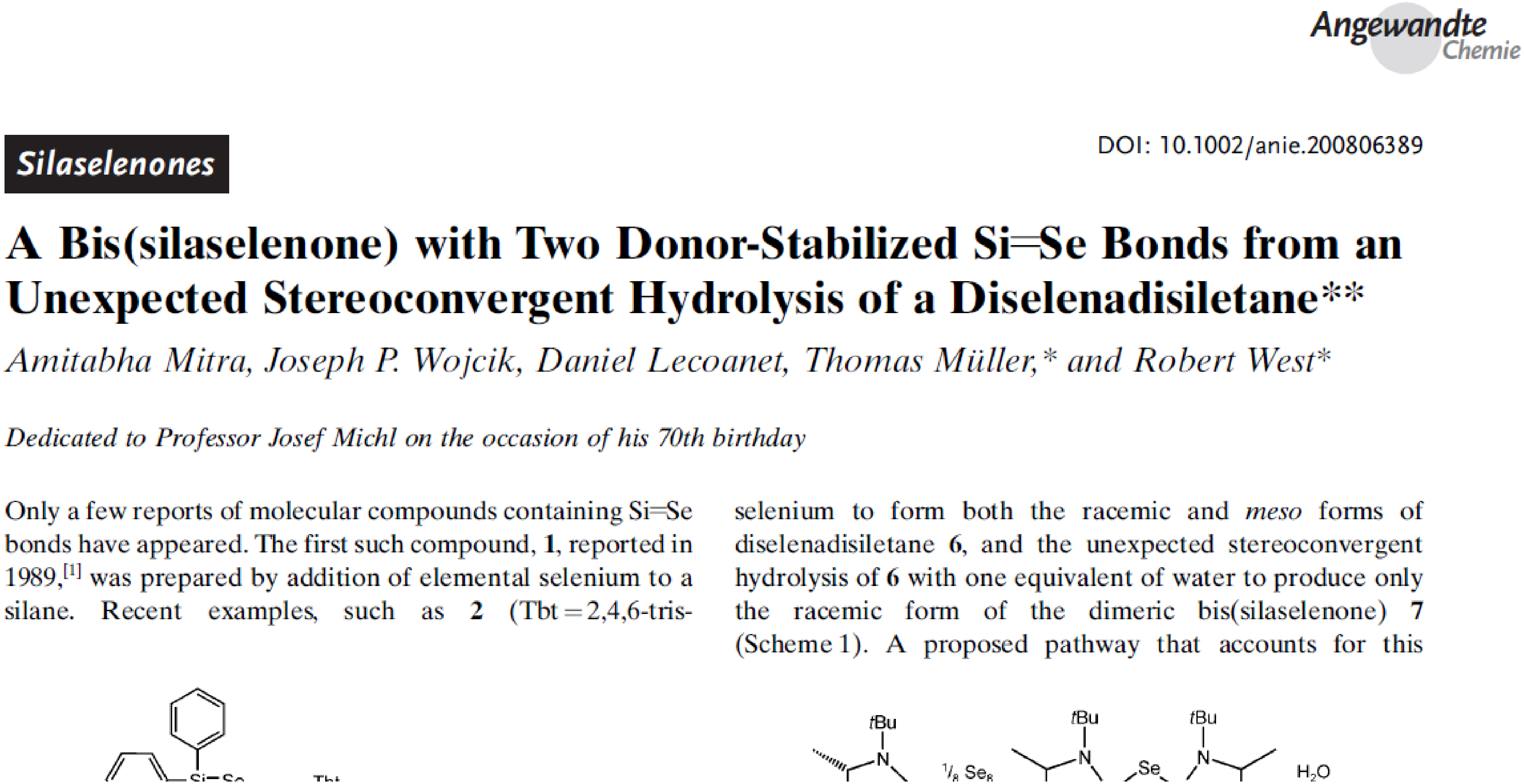
The First Kinetically Stabilized Germanethiones and Germaneselones: Syntheses, Structures, and Reactivities

Tsuyoshi Matsumoto,[†] Norihiro Tokitoh,*[,‡] and Renji Okazaki*[,§]

*Contribution from the Department of Chemistry, Graduate School of Science, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Received April 12, 1999

Abstract: The first kinetically stabilized germanethiones (germanium−sulfur double-bond species) and germaneselones (germanium−selenium double-bond species) were synthesized. Dechalcogenation of the novel 1,2,3,4,5-tetrachalcogenagermolane Tbt(Tip)GeX_4 (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl, X = S or Se) with 3 molar equiv of triphenylphosphine gave diaryl-substituted



Angewandte Chemie

DOI: 10.1002/anie.200806389

Silaselenones

A Bis(silaselenone) with Two Donor-Stabilized Si=Se Bonds from an Unexpected Stereoconvergent Hydrolysis of a Diselenadisiletane**

Amitabha Mitra, Joseph P. Wojcik, Daniel Lecoanet, Thomas Müller, and Robert West**

Dedicated to Professor Josef Michl on the occasion of his 70th birthday

Only a few reports of molecular compounds containing Si=Se bonds have appeared. The first such compound, **1**, reported in 1989,[1] was prepared by addition of elemental selenium to a silane. Recent examples, such as **2** (Tbt = 2,4,6-tris-

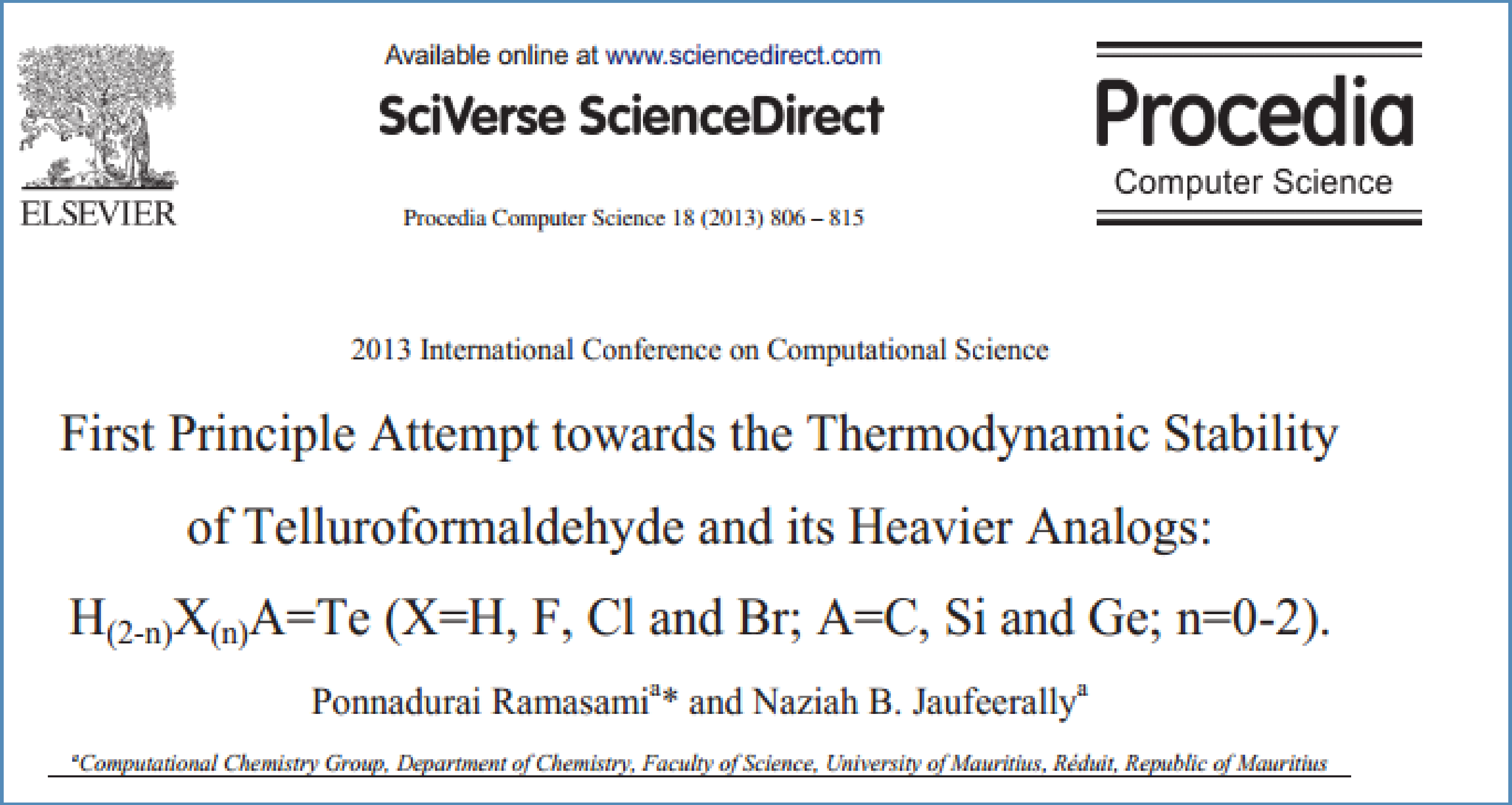
selenium to form both the racemic and *meso* forms of diselenadisiletane **6**, and the unexpected stereoconvergent hydrolysis of **6** with one equivalent of water to produce only the racemic form of the dimeric bis(silaselenone) **7** (Scheme 1). A proposed pathway that accounts for this

Conclusions from literature…

Heavy ketones and telluro-ketones synthesized and isolated so far are based on the kinetic stabilization of the A=E bond by the use of bulky rigid protecting groups.

Does this means that the simple, unprotected telluro-ketones are unstable compared to those kinetically protected ones?

Our Response to the Queries



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Procedia Computer Science 18 (2013) 806 – 815

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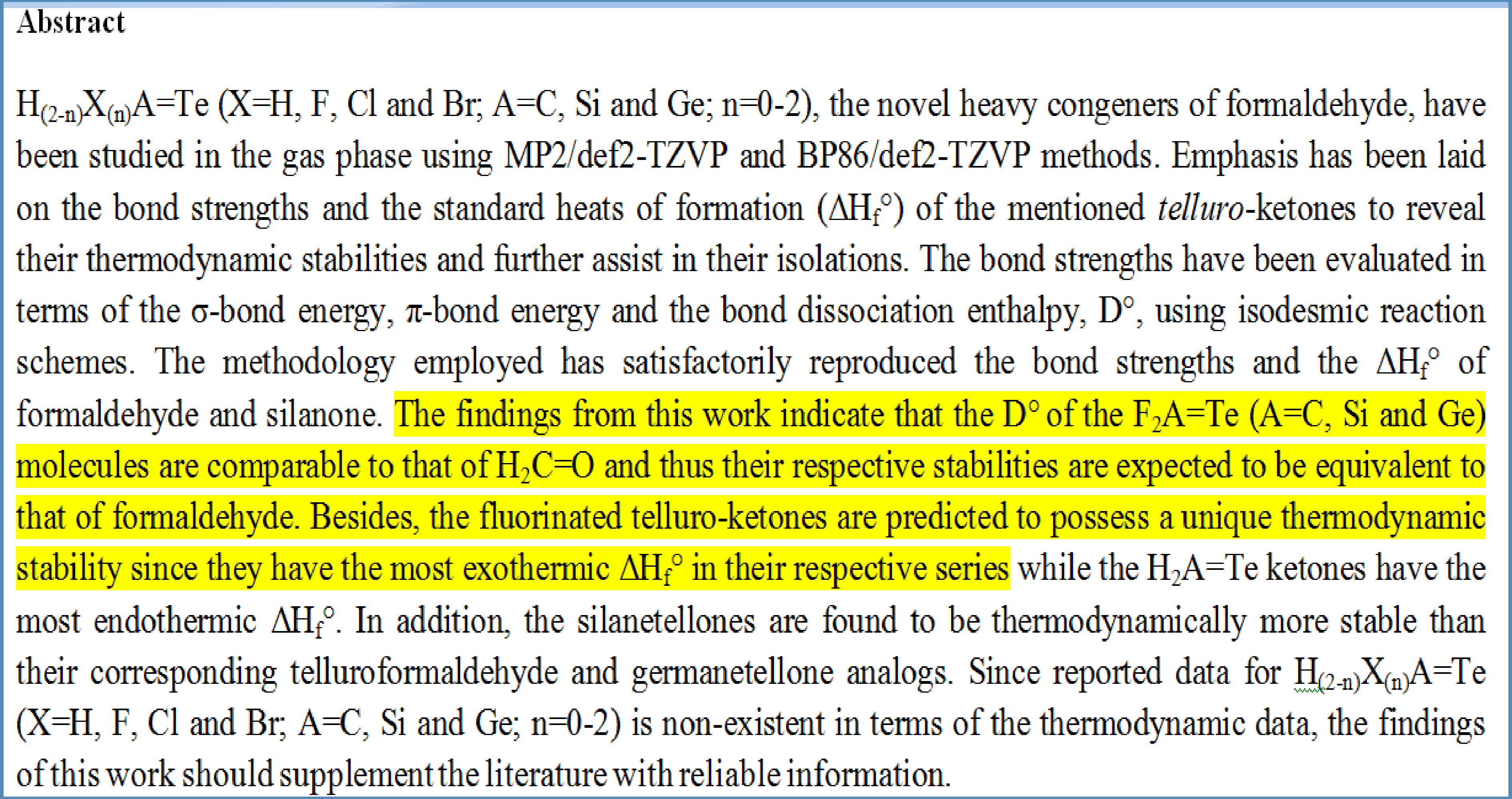
First Principle Attempt towards the Thermodynamic Stability of Telluroformaldehyde and its Heavier Analogs: $H_{(2-n)}X_{(n)}A=Te$ (X=H, F, Cl and Br; A=C, Si and Ge; n=0-2).

Ponnadurai Ramasami[a]* and Naziah B. Jaufeerally[a]

[a]*Computational Chemistry Group, Department of Chemistry, Faculty of Science, University of Mauritius, Réduit, Republic of Mauritius*

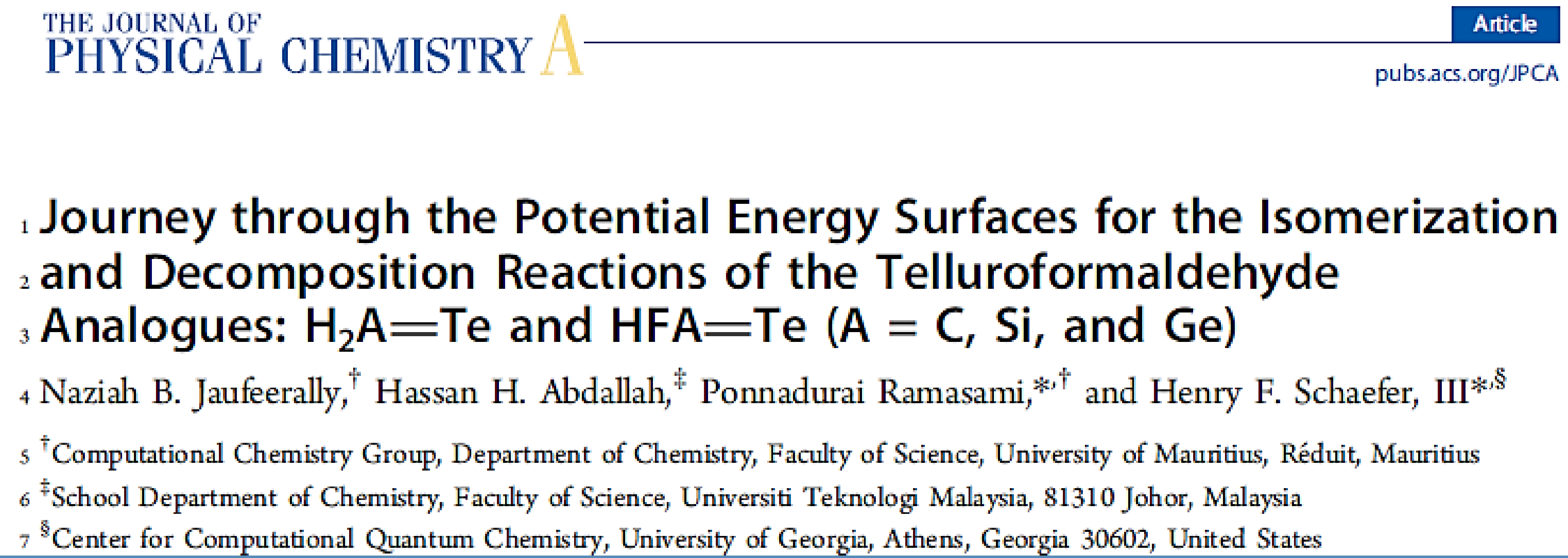
Our Response to the Queries



Abstract

$H_{(2\text{-}n)}X_{(n)}A{=}Te$ (X=H, F, Cl and Br; A=C, Si and Ge; n=0-2), the novel heavy congeners of formaldehyde, have been studied in the gas phase using MP2/def2-TZVP and BP86/def2-TZVP methods. Emphasis has been laid on the bond strengths and the standard heats of formation (ΔH_f°) of the mentioned *telluro*-ketones to reveal their thermodynamic stabilities and further assist in their isolations. The bond strengths have been evaluated in terms of the σ-bond energy, π-bond energy and the bond dissociation enthalpy, D°, using isodesmic reaction schemes. The methodology employed has satisfactorily reproduced the bond strengths and the ΔH_f° of formaldehyde and silanone. The findings from this work indicate that the D° of the $F_2A{=}Te$ (A=C, Si and Ge) molecules are comparable to that of $H_2C{=}O$ and thus their respective stabilities are expected to be equivalent to that of formaldehyde. Besides, the fluorinated telluro-ketones are predicted to possess a unique thermodynamic stability since they have the most exothermic ΔH_f° in their respective series while the $H_2A{=}Te$ ketones have the most endothermic ΔH_f°. In addition, the silanetellones are found to be thermodynamically more stable than their corresponding telluroformaldehyde and germanetellone analogs. Since reported data for $H_{(2\text{-}n)}X_{(n)}A{=}Te$ (X=H, F, Cl and Br; A=C, Si and Ge; n=0-2) is non-existent in terms of the thermodynamic data, the findings of this work should supplement the literature with reliable information.

Our Response to the Queries



THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

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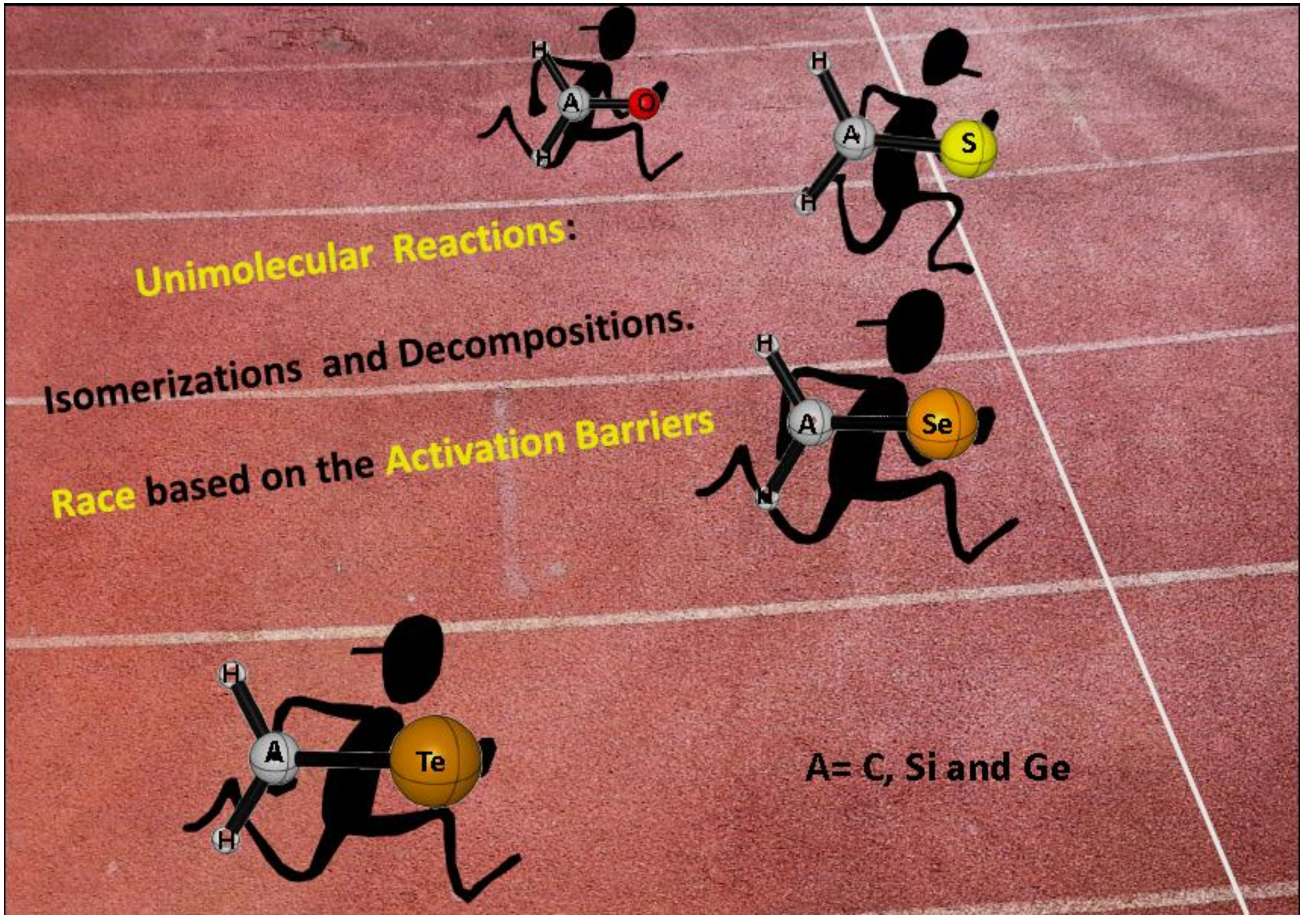
Journey through the Potential Energy Surfaces for the Isomerization and Decomposition Reactions of the Telluroformaldehyde Analogues: $H_2A{=}Te$ and $HFA{=}Te$ ($A = C$, Si, and Ge)

Naziah B. Jaufeerally,[†] Hassan H. Abdallah,[‡] Ponnadurai Ramasami,*[,†] and Henry F. Schaefer, III*[,§]

[†]Computational Chemistry Group, Department of Chemistry, Faculty of Science, University of Mauritius, Réduit, Mauritius
[‡]School Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor, Malaysia
[§]Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602, United States

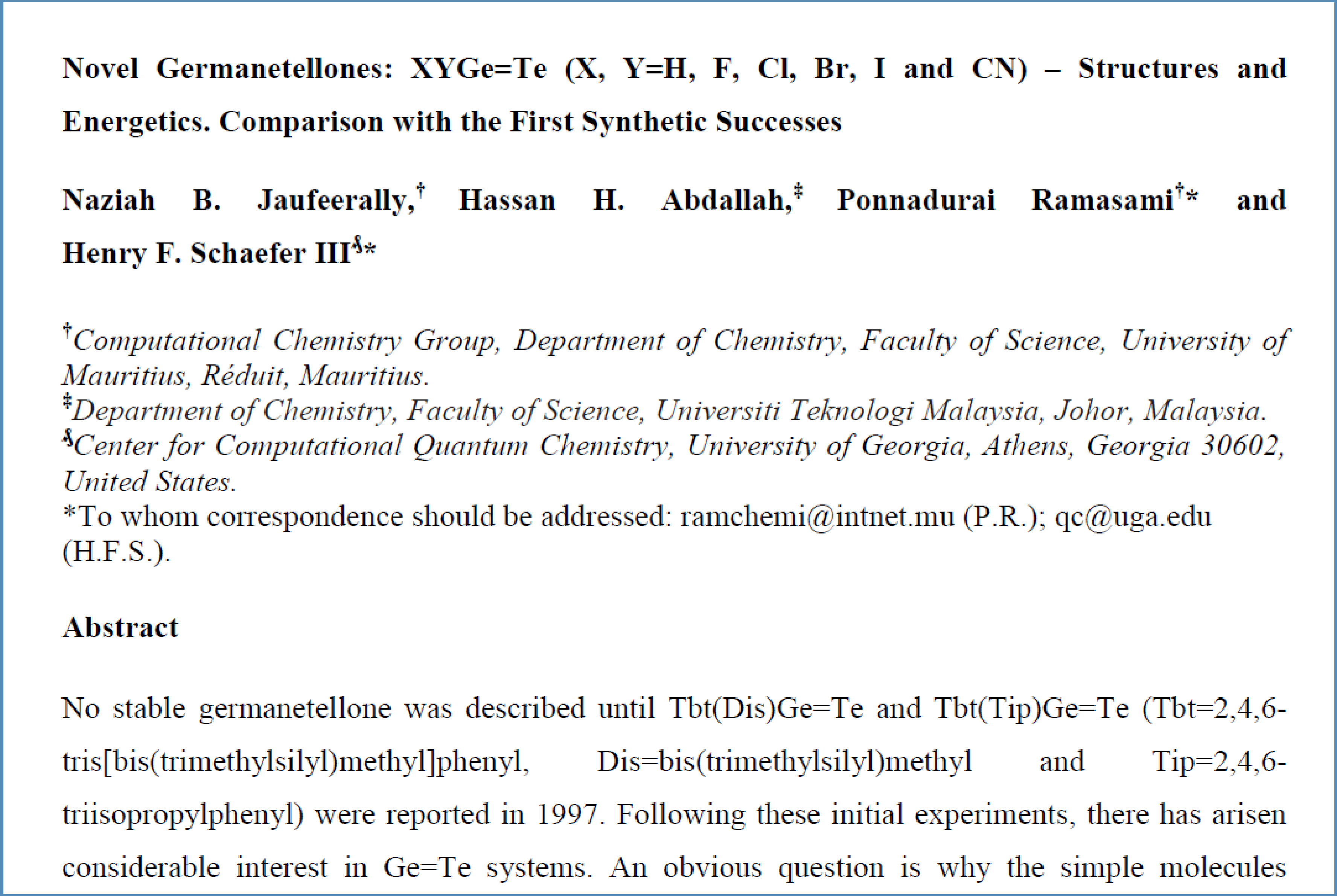
Our Response to the Queries



A = Si < A = Ge. However, the telluro-ketones are found to be kinetically and thermodynamically more stable than their corresponding lighter chalcogen analogues.

Overall, telluroformaldehyde and silanetellone are kinetically and thermodynamically more stable with respect to the unimolecular reactions studied. However, germatellone is shown to be more reactive. This can be due to the fact that

Our Response to the Queries



Novel Germanetellones: XYGe=Te (X, Y=H, F, Cl, Br, I and CN) – Structures and Energetics. Comparison with the First Synthetic Successes

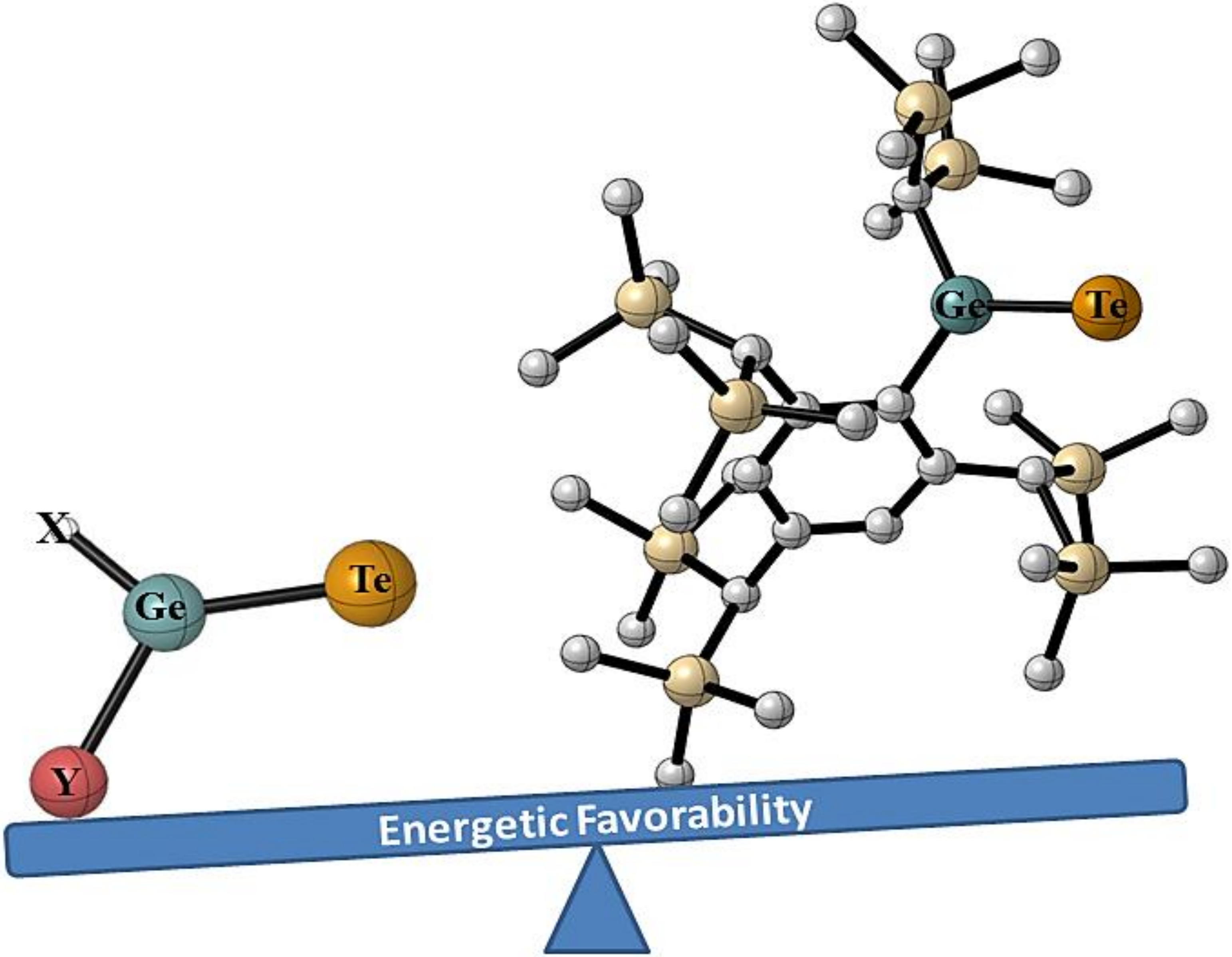
Naziah B. Jaufeerally,[†] Hassan H. Abdallah,[‡] Ponnadurai Ramasami[†*] and Henry F. Schaefer III[§*]

[†] *Computational Chemistry Group, Department of Chemistry, Faculty of Science, University of Mauritius, Réduit, Mauritius.*
[‡] *Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, Johor, Malaysia.*
[§] *Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602, United States.*
*To whom correspondence should be addressed: ramchemi@intnet.mu (P.R.); qc@uga.edu (H.F.S.).

Abstract

No stable germanetellone was described until Tbt(Dis)Ge=Te and Tbt(Tip)Ge=Te (Tbt=2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dis=bis(trimethylsilyl)methyl and Tip=2,4,6-triisopropylphenyl) were reported in 1997. Following these initial experiments, there has arisen considerable interest in Ge=Te systems. An obvious question is why the simple molecules

Our Response to the Queries



Further Objectives

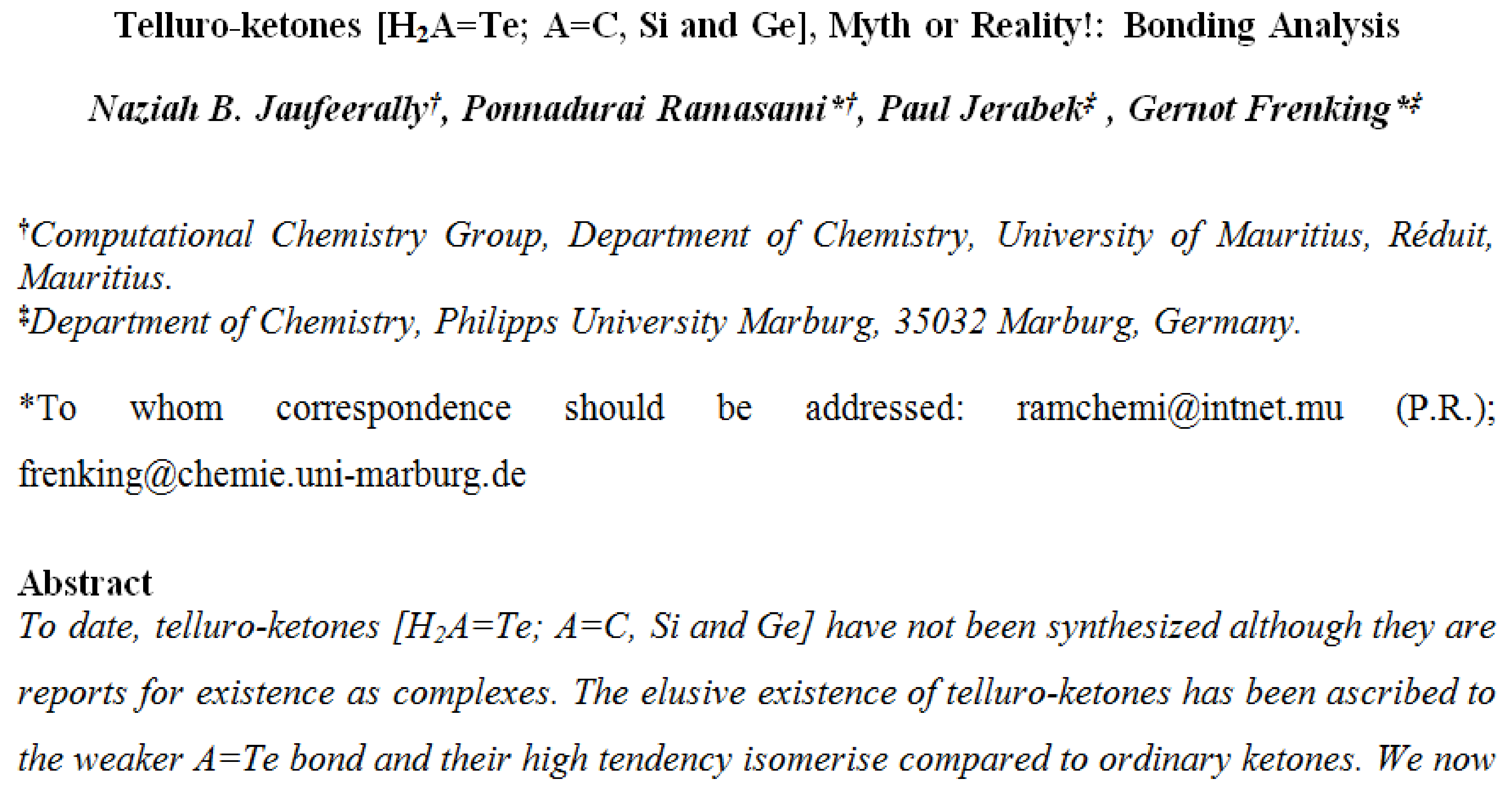
Existence of Telluro-ketones is

Not a Myth

But

a Reality!

In view of this, we are currently working on the following manuscript



Telluro-ketones [H_2A=Te; A=C, Si and Ge], Myth or Reality!: Bonding Analysis

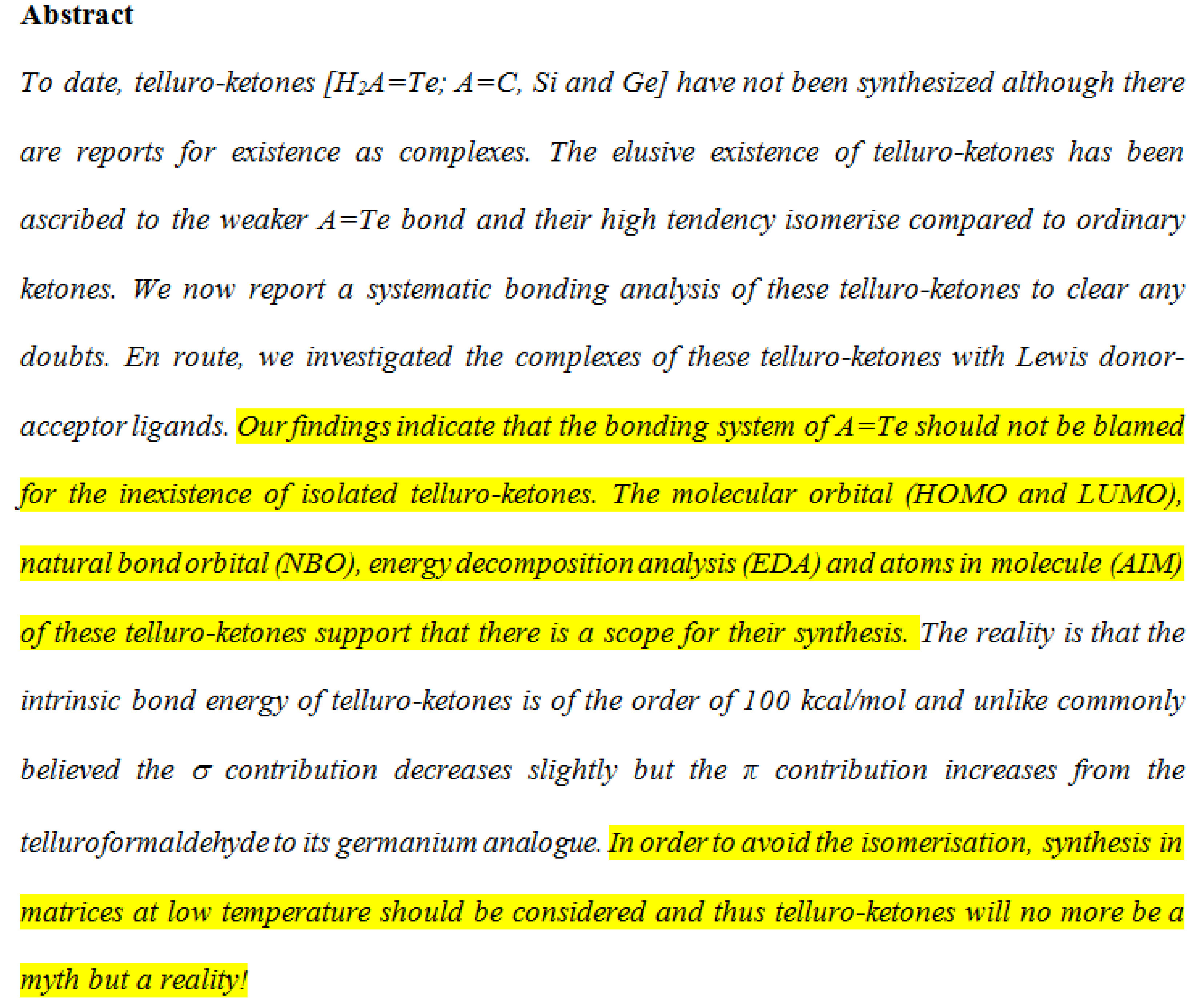
Naziah B. Jaufeerally[†], *Ponnadurai Ramasami**[†], *Paul Jerabek*[‡] , *Gernot Frenking**[‡]

[†]*Computational Chemistry Group, Department of Chemistry, University of Mauritius, Réduit, Mauritius.*
[‡]*Department of Chemistry, Philipps University Marburg, 35032 Marburg, Germany.*

*To whom correspondence should be addressed: ramchemi@intnet.mu (P.R.); frenking@chemie.uni-marburg.de

Abstract

To date, telluro-ketones [H_2A=Te; A=C, Si and Ge] have not been synthesized although they are reports for existence as complexes. The elusive existence of telluro-ketones has been ascribed to the weaker A=Te bond and their high tendency isomerise compared to ordinary ketones. We now



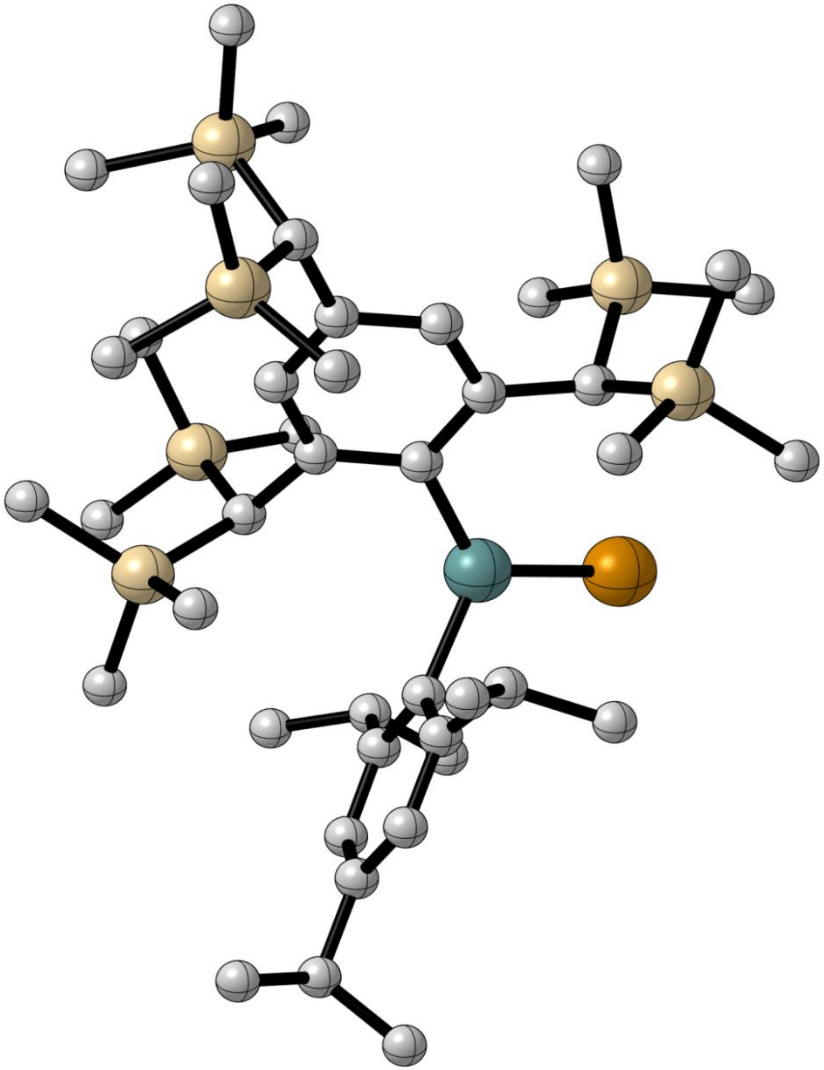
Abstract

To date, telluro-ketones [H_2A=Te; A=C, Si and Ge] have not been synthesized although there are reports for existence as complexes. The elusive existence of telluro-ketones has been ascribed to the weaker A=Te bond and their high tendency isomerise compared to ordinary ketones. We now report a systematic bonding analysis of these telluro-ketones to clear any doubts. En route, we investigated the complexes of these telluro-ketones with Lewis donor-acceptor ligands. Our findings indicate that the bonding system of A=Te should not be blamed for the inexistence of isolated telluro-ketones. The molecular orbital (HOMO and LUMO), natural bond orbital (NBO), energy decomposition analysis (EDA) and atoms in molecule (AIM) of these telluro-ketones support that there is a scope for their synthesis. The reality is that the intrinsic bond energy of telluro-ketones is of the order of 100 kcal/mol and unlike commonly believed the σ contribution decreases slightly but the π contribution increases from the telluroformaldehyde to its germanium analogue. In order to avoid the isomerisation, synthesis in matrices at low temperature should be considered and thus telluro-ketones will no more be a myth but a reality!

Further Studies

Stabilization of the C=Te, Si=Te and Ge=Te double bonds

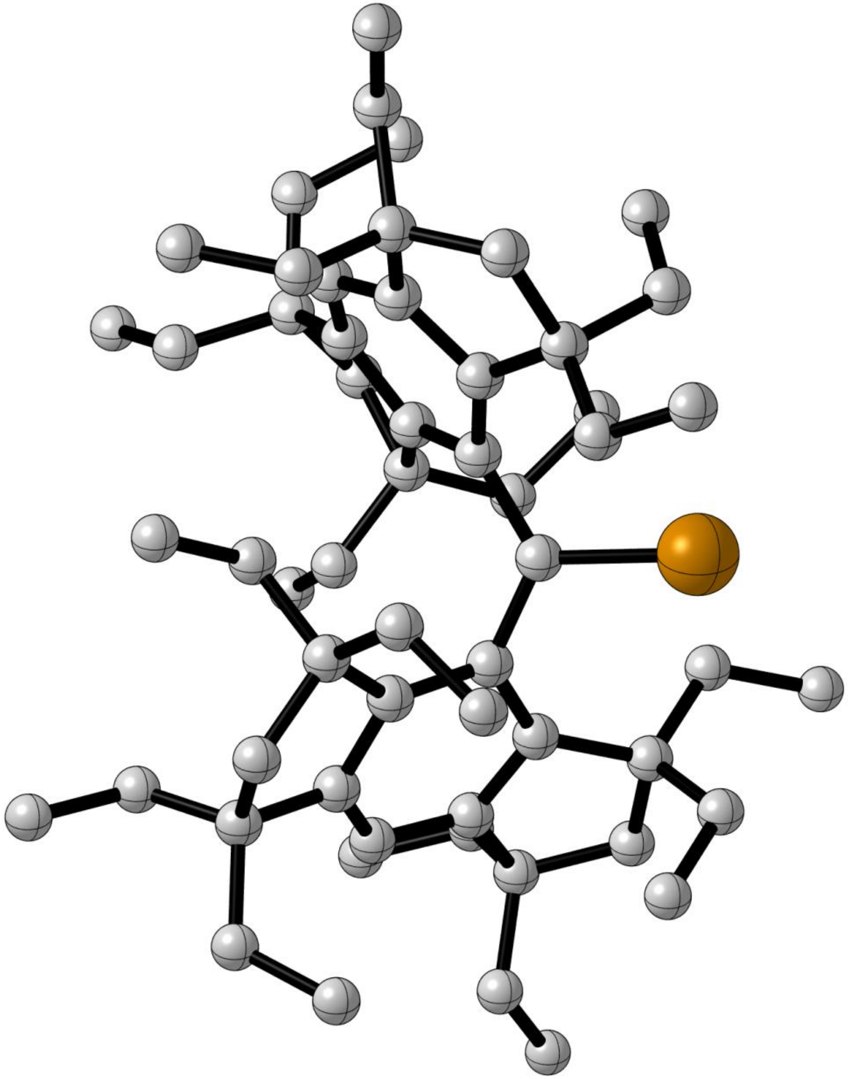
With the help of rigid and bulky protecting groups



Modeled from the 1st synthetic success of germanetellone reported in JACS

Stabilization of the C=Te, Si=Te and Ge=Te double bonds

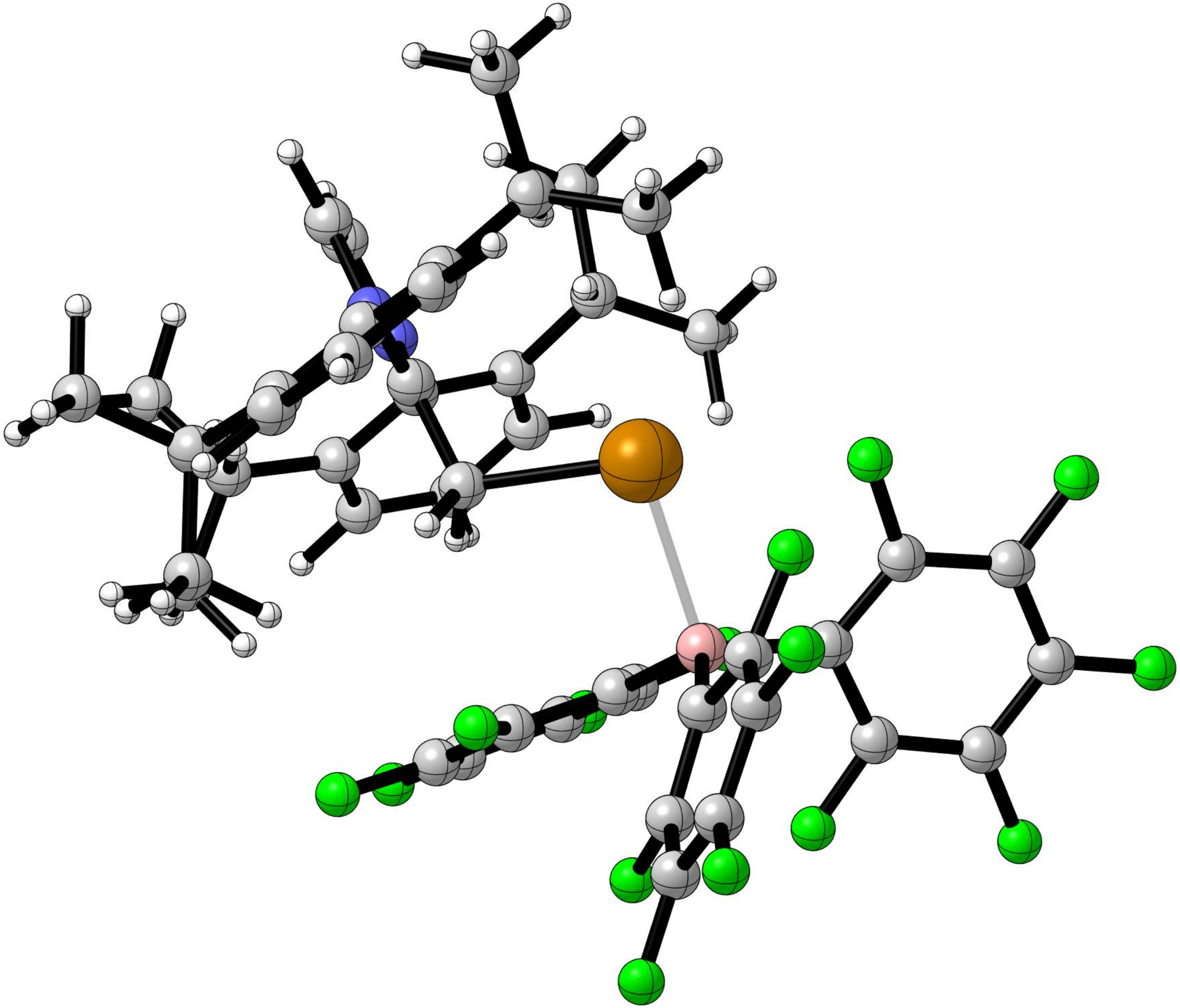
With the help of rigid and bulky protecting groups



Modeled from the 1st synthetic success of germanone reported in Nature Chemistry

Stabilization of the C=Te, Si=Te and Ge=Te double bonds

With the help of Lewis donor-acceptor ligands



Conclusions

- ✓ Since state-of-the-art computations have been carried out, findings of this work can serve as a good reference and assist experimentalists to

- ✓ synthesize, characterize

- ✓ and further explore the properties of these novel telluro-ketones

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